

**Longman
Certificate
Notes**

SI Units

Chemistry

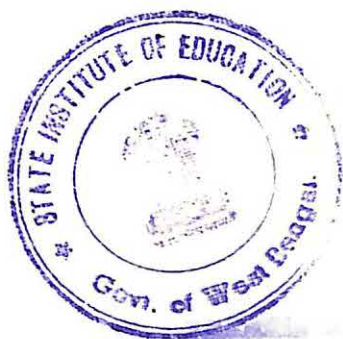


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Longman Certificate Notes

Chemistry

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Longman

LONGMAN GROUP LIMITED
LONDON

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1 The structure of matter

Atomic theory

Chemistry is a study of the substances in the universe, to find out:

a what they are made of;

b how they combine with each other;

c how they and their reactions are affected by physical influences.

Philosophers of most of the ancient civilisations believed that matter was composed of fundamental particles, which we now call atoms, joined together in different ways. There have been many speculations through the centuries as to the nature of these particles, and there was one period (the Middle Ages) when the quest for riches became more important than the quest for truth; alchemists searched for a method of turning other metals into gold. This quest was not a total waste because it produced many of the familiar experimental techniques used today. However, it was not until shortly after 1800 that ideas about atomic structure were consolidated by an English chemist, John Dalton.

The main points of Dalton's Atomic Theory were:

a Elements are composed of atoms;

b atoms are very small and indivisible;

c atoms of the same element are alike and atoms of different elements are not alike;

d atoms can join together in small whole numbers to form compound atoms (now called molecules).

Although Dalton's ideas are to a large extent outmoded by modern theories, they still serve as an adequate explanation of some of the fundamental principles of chemistry.

The chemical laws

These laws give support to Dalton's Atomic Theory.

THE LAW OF CONSERVATION OF MASS

Matter can be neither created nor destroyed. There are many reactions which can be used to prove this, e.g. the apparatus in fig. 1 contains

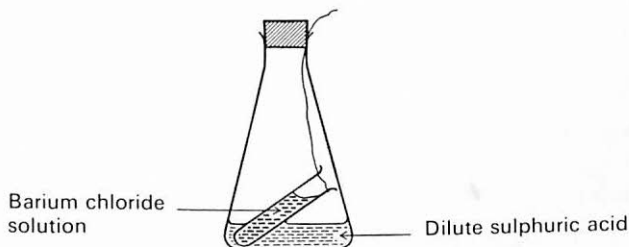


fig. 1

dilute sulphuric acid and barium chloride solution. It is weighed, shaken to mix the reagents, which react to form a white precipitate, and then weighed again. No change in weight occurs.

Note: Einstein showed that matter can be destroyed, but when this is done by a nuclear reaction the matter is transferred into energy.

THE LAW OF CONSTANT COMPOSITION

A chemical compound, no matter how formed, always contains the same elements in the same proportion by weight. The usual method of proving this is to make black copper oxide by three different methods.

- a Copper (II) nitrate $\xrightarrow{\text{heat}}$ black copper (II) oxide.
- b Copper (II) carbonate $\xrightarrow{\text{heat}}$ black copper (II) oxide.
- c Copper (II) sulphate solution + sodium hydroxide solution $\xrightarrow{\text{heat}}$ black copper (II) oxide.

The samples so formed are analysed by reduction (see p. 28) and it is found that within the limits of experimental error the ratio of the weights of copper and oxygen in each sample is the same. This is the ratio of the combining weights of copper and oxygen.

Atoms, molecules, elements and compounds

An *atom* is the smallest part of an element that can take part in a chemical reaction.

An *element* is a substance which cannot be obtained in a simpler form by chemical means.

A *molecule* is the smallest part of any substance which can have a separate existence.

A *compound* is a substance formed by the chemical combination of two or more elements in a definite proportion by weight.

Thus, matter as we meet it in the laboratory and in everyday life consists of elements, compounds and mixtures of these.

Elements consist of atoms which are all the same.

Compounds consist of molecules which are all the same.



Types of reaction

Combination Iron + sulphur = iron sulphide

Decomposition Mercury (II) oxide = mercury + oxygen ↑

Double decomposition

Silver nitrate + sodium chloride = sodium nitrate + silver chloride↓

Oxidation Magnesium + oxygen = magnesium oxide

Reduction Copper (II) oxide + hydrogen = copper + water

Neutralisation

Sodium hydroxide + hydrochloric acid = sodium chloride + water

Symbols and formulae

Every chemical reaction may be represented by an equation either in words as above or by using symbols and formulae. The latter constitute a form of chemical shorthand, each different element being represented by its initial letter or the initial letter and a small letter e.g. Carbon C; Calcium Ca

In some cases the symbol is taken from the name of the substance in another language e.g.

Sodium (Natrium) Na; Copper (Cuprum) C

Each element has a valency which is its combining number and is represented by a small whole number. Some elements have more than one valency e.g. copper has valencies of 1 and 2. Compounds of copper were formerly written as cuprous oxide and cupric oxide. To-day these are simplified by writing copper I oxide and copper II oxide. The Roman numerals indicating the valency of the metal in the compound also applies to iron, mercury, lead and manganese. Formulae can be written using symbols and valencies, e.g.

Sodium chloride

Sodium	Na	valency 1 } combine in equal numbers to give valency 1 } the formula NaCl.
Chlorine	Cl	

Calcium chloride

Calcium	Ca	valency 2 } combine in the ratio 1 : 2 to give the valency 1 } formula CaCl ₂ .
Chlorine	Cl	

Copper (II) oxide

Copper	Cu	valency 2 } combine in equal numbers to give valency 2 } the formula CuO.
Oxygen	O	

Aluminium oxide

Aluminium	Al	valency 3 } combine in the ratio 2 : 3 to give the valency 2 } formula Al ₂ O ₃ .
Oxygen	O	

In addition to simple elements, compounds contain radicals or groups of atoms which cannot exist on their own, e.g.

Copper (II) sulphate

Copper	Cu	valency 2 } combine in equal numbers to give valency 2 } the formula CuSO ₄ .
Sulphate	-SO ₄	

Calcium hydroxide

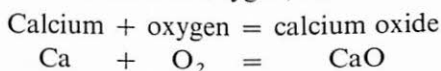
Calcium Ca valency 2 } combine in the ratio 1:2 to give the
Hydroxide -OH valency 1 } formula **Ca(OH)₂**.

Note: In the formula Ca(OH)_2 a bracket surrounds the -OH radical and the figure 2 governs everything inside the bracket.

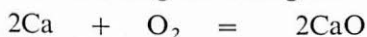
Equations

An equation has on the left hand side the reagents, and on the right hand side the products of the reaction. Thus it represents what takes place when chemical substances react. (It should be noted that a theoretical equation does not guarantee that such a reaction will take place in practice.) The names of the reactants and products should first be written down. The formula of each compound should then be worked out, put in the appropriate place and the equation balanced. To do this it may be treated in a similar fashion to an algebraic equation; there must be the same number of the same elements on each side, e.g.

a In the reaction of calcium with oxygen, calcium oxide is formed.



This, as it stands, is not balanced; there are two oxygen atoms on the left and only one on the right. It can be balanced by doubling CaO, which then necessitates doubling Ca. This gives.



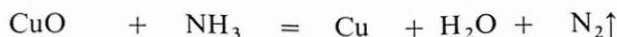
Note: It is not possible simply to double the O atom, giving CaO_2 , since this completely changes the composition of calcium oxide.

b The reaction of ammonia with copper oxide produces copper, water and nitrogen.

Words

Copper II oxide + ammonia = copper + water + nitrogen

Unbalanced



Balanced



The arrow pointing upwards indicates that nitrogen is a gas.

c The reaction of sodium sulphate solution with lead (II) nitrate solution produces sodium nitrate and lead (II) sulphate.

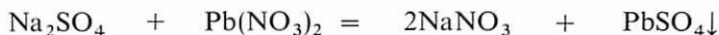
Words

Sodium sulphate + lead (II) nitrate = sodium nitrate + lead (II) sulphate↓

Unbalanced

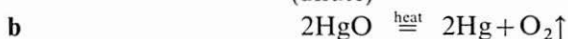
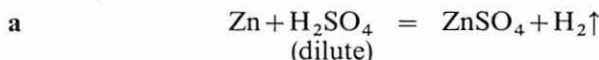


Balanced



The arrow pointing downwards shows that lead (II) sulphate is insoluble and is formed as a precipitate.

The equations above show only the *compounds* involved in the reactions. The conditions for reaction, such as temperature, concentration or the necessity of using a catalyst, are often shown, e.g.



Atomic structure and compound formation

Dalton's concept of the atom was completely accepted for a time but various investigations produced evidence that atoms did in fact contain smaller particles. These are the *electron*, the *proton* and the *neutron*.

Particle	Relative mass	Electrical charge
Electron	0	-1
Proton	1	+1
Neutron	1	0

Note:

a The electron actually has a mass about $\frac{1}{1850}$ of that of a proton.

b These masses were based on the scale on which the oxygen atom weighs 16 units, and are now based on a scale on which $^{12}\text{C} = 12$ (see p. 56).

Atomic structure

The atom is composed of a positive nucleus, containing protons and neutrons, with negative electrons spinning in orbits or shells around it.

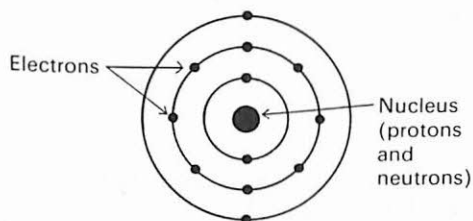


fig. 2 The magnesium atom

(The modern view is that there is simply an electron cloud surrounding the nucleus.)

Since electrons contribute very little weight, the mass of the atom is concentrated in the nucleus.

To maintain the electrical neutrality of the atom,

$$\text{number of electrons} = \text{number of protons}$$

This is called the *atomic number* of the atom.

Several attempts were made to classify the elements, and it was eventually found that the simplest classification was by atomic number, giving rise to what is known as the *Periodic Classification of the Elements*. The table below indicates how the electrons are distributed in shells around the nucleus, the innermost being called the K shell, the next the L shell, etc. There is a maximum number of electrons that can be contained in each shell. This is 2 for the K shell and 8 each for the L and M shells.

The total number of protons and neutrons in each atom is effectively the weight of the atom, and is known as the *mass number* (see page 56).

TABLE SHOWING STRUCTURES OF THE FIRST 20 ELEMENTS

Element	Symbol	Electrons in shells				Protons p	Neutrons n	Mass number p + n
		K	L	M	N			
Hydrogen	H	1				1	0	1
Helium	He	2				2	2	4
Lithium	Li	2	1			3	4	7
Beryllium	Be	2	2			4	5	9
Boron	B	2	3			5	6	11
Carbon	C	2	4			6	6	12
Nitrogen	N	2	5			7	7	14
Oxygen	O	2	6			8	8	16
Fluorine	F	2	7			9	10	19
Neon	Ne	2	8			10	10	20
Sodium	Na	2	8	1		11	12	23
Magnesium	Mg	2	8	2		12	12	24
Aluminium	Al	2	8	3		13	14	27
Silicon	Si	2	8	4		14	14	28
Phosphorus	P	2	8	5		15	16	31
Sulphur	S	2	8	6		16	16	32
Chlorine	Cl	2	8	7		17	18	35
Argon	Ar	2	8	8		18	22	40
Potassium	K	2	8	8	1	19	20	39
Calcium	Ca	2	8	8	2	20	20	40

Note:

a In each case the sum of the electrons = the number of protons.

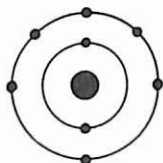
b The number of neutrons is not predictable and need not be memorised. In the Periodic Table the rows are known as periods and the columns as groups.

The first 20 elements are arranged thus:

H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca						

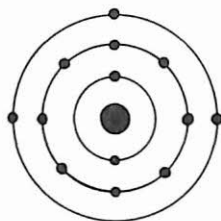
If you memorise this arrangement you will be able to recall the electronic structures of specific elements quickly.

a The electronic structure of oxygen. Oxygen is in the 2nd period, \therefore the K shell is full with 2 electrons. Oxygen is in the 6th group, \therefore there are 6 electrons in the L shell. Thus the structure of the oxygen atom is



or 2.6

b The electronic structure of aluminum. Aluminium is in the 3rd period, \therefore K and L shells are full, with 2 and 8 electrons respectively. Aluminium is in the 3rd group, \therefore there are 3 electrons in the M shell. Thus the structure of the aluminium atom is



or 2.8.3

The inert gases and compound formation

The elements at the extreme right of each period are known as the inert gases and have unique properties. They are:

helium 2; neon 2.8; argon 2.8.8.

- 1 The inert gases do not react to any appreciable extent. They are very stable.
- 2 The inert gases have complete outer shells of electrons.
- 3 Elements in general achieve stability by reaction with other elements, e.g.

Sodium (reactive metal)	}	sodium chloride (stable compound)
Chlorine (reactive gas)		
- 4 It is therefore assumed that this stability is achieved by the atom acquiring an inert gas structure.

RULE FOR COMPOUND FORMATION

When compounds are formed, the atoms concerned lose or gain electrons so that their outer shell has the same structure as that of the nearest inert gas. This can be done in two ways, either by sharing electrons or by transferring them completely from one atom to another.

Note: Only the outer electrons are involved in compound formation.

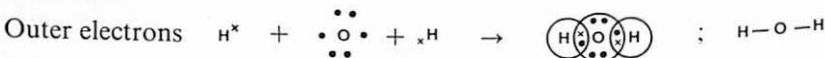
ELECTRON SHARING: COVALENCY

a Chlorine gas, Cl_2 , consists of diatomic molecules.



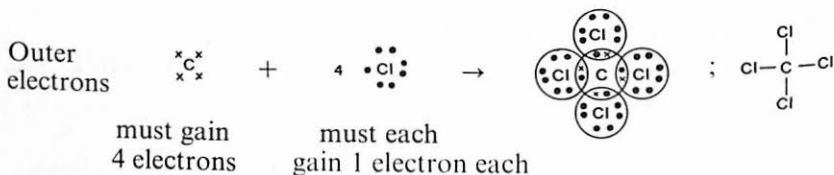
Each chlorine atom has seven electrons on its outer shell. The nearest inert gas is argon, with eight on its outer shell, so according to the rule of compound formation each chlorine atom must gain one electron. This can be done only by sharing, and the pair of mutually shared electrons constitutes a covalent bond which is represented by a stroke thus: $\text{Cl}-\text{Cl}$.

b Water, H_2O , consists of two atoms of hydrogen and one atom of oxygen per molecule.

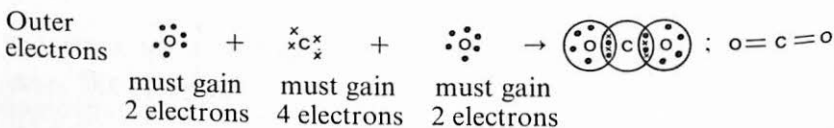


Each hydrogen atom has one electron on its outer shell and must therefore gain one more electron to attain the outer structure of helium (the nearest inert gas). The oxygen atom has six electrons on its outer shell and must gain two electrons to attain the outer structure of neon.

c Carbon tetrachloride, CCl_4 , consists of one atom of carbon and four atoms of chlorine per molecule.

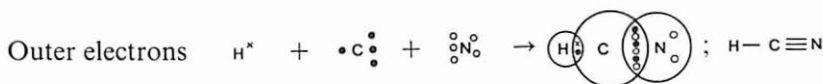


d Carbon dioxide, CO_2 , consists of one atom of carbon and two atoms of oxygen per molecule.



In this case two pairs of shared electrons constitute the bond on each side of the carbon atom. Each of these is a double covalent bond.

e Hydrogen cyanide, HCN, consists of one atom of hydrogen, one of carbon and one of nitrogen.



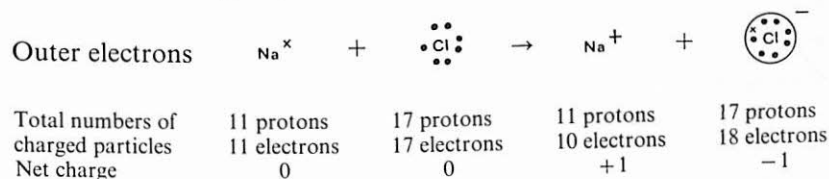
This shows the existence and formation of a triple covalent bond.

Properties of covalent compounds

- 1 They are low melting solids, volatile liquids or gases.
- 2 They do not conduct electricity.
- 3 They are composed mainly of non-metallic elements joined together.
- 4 Their crystals, when they are in the solid state, are composed of individual *molecules* joined loosely together.
- 5 Their reactions are usually slow.

ELECTRON TRANSFER: ELECTROVALENCY

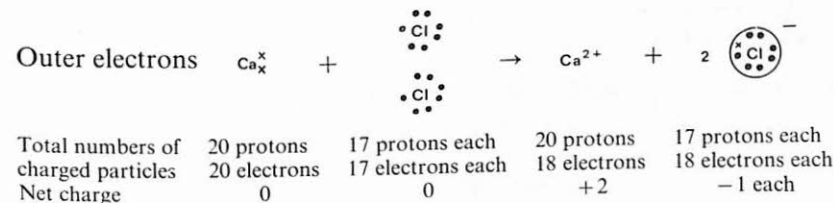
a Sodium chloride, NaCl



The sodium atom loses its one outer electron to attain the same outer structure as neon. The chlorine atom gains one electron to attain the same outer structure as argon.

The electron referred to is simply transferred from the sodium atom to the chlorine atom and since the number of positive protons in the nucleus is unchanged in each case, each atom acquires a charge and becomes known as an *ion*.

b Calcium chloride, CaCl_2



This is a similar situation, except that the calcium atom has two electrons to lose and each chlorine atom gains one of them.

Note: Positive ions are called *cations* and negative ions are called *anions*.

Properties of electrovalent (ionic) compounds

- 1 They are usually solids with a high melting point.
- 2 They conduct electricity when in solution or in the fused (molten) state, due to the ions, which are set free under these conditions.
- 3 The elements present in simpler electrovalent compounds are usually very electropositive metals and very electronegative non-metals, e.g. NaCl.

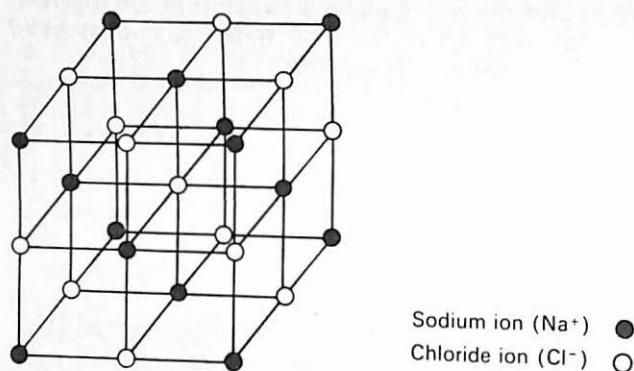


fig. 3 A sodium chloride crystal lattice

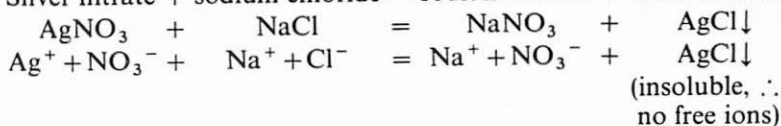
- 4 Electrovalent compounds are *not* composed of molecules. The ions present are to a certain extent independent of each other and are arranged in a network or crystal lattice, held together by the attraction between unlike charges. The ions can only vibrate and cannot move freely in this lattice (fig. 3). In order that the ions may take part in chemical reactions they must be freed, and this is done by dissolving the substance in water or by melting it.
- 5 Their reactions are fast since they are caused by the attraction between cations from one compound and anions from another compound.

Ionic reactions and ionic equations

When ionic compounds dissolve in water the ions are set free and when two such solutions are mixed, a reaction takes place if there is a tendency for a compound, whose ions are not free, to be formed.

PRECIPITATION REACTIONS

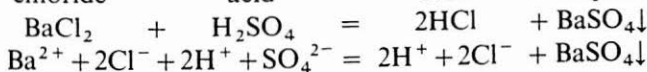
a Silver nitrate + sodium chloride = sodium nitrate + silver chloride



Nitrate (NO_3^-) and sodium (Na^+) ions are unchanged. The net change is $\text{Ag}^+ + \text{Cl}^- = \text{AgCl}\downarrow$. This is useful since:—

- i it gives a concise statement of what actually happens;
- ii it is general and covers every case where Ag^+ and Cl^- meet.

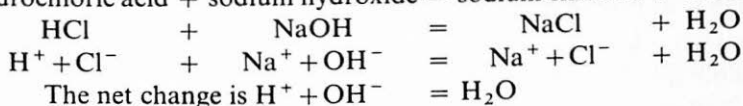
b Barium chloride + sulphuric acid = hydrochloric acid + barium sulphate



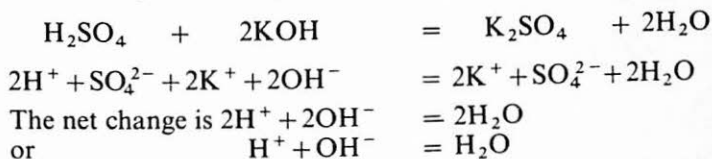
The net change is $\text{Ba}^{2+} + \text{SO}_4^{2-} = \text{BaSO}_4\downarrow$

NEUTRALISATIONS

a Hydrochloric acid + sodium hydroxide = sodium chloride + water



b Sulphuric acid + potassium hydroxide = sulphate potassium + water

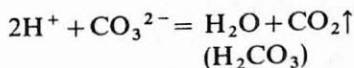
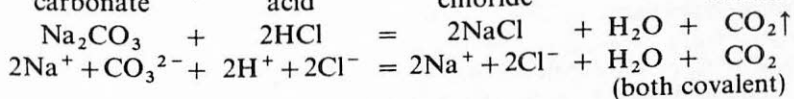


Thus this ionic equation represents the reaction that takes place when any acid and any alkali react.

Note: Although pure water is a covalent substance it ionises when impure.

REACTION BETWEEN ACIDS AND CARBONATES

Sodium carbonate + hydrochloric acid = sodium chloride + water + carbon dioxide

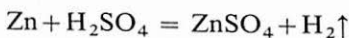


The electrochemical series (activity series)

If a metal A can displace metal B from a solution of one of its salts then A is said to be more electropositive than B, e.g.

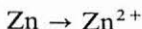
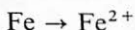


Iron is more electropositive than copper. This can be extended to other atoms and ions, e.g.



Zinc is more electropositive than hydrogen.

In each of these reactions the more electropositive element has been ionised and has therefore lost electrons, thus:



Electropositivity is thus the ability of an atom to lose electrons, and the opposite of this is *electronegativity* – the ability to gain electrons. The *electrochemical series* is a series of elements or ions arranged with the most electropositive at the top and the least electropositive (or the most electronegative) at the bottom.

THE ELECTROCHEMICAL SERIES (E.C.S.) (ACTIVITY SERIES)

Potassium	$\text{K} \rightarrow \text{K}^+$	most electropositive
Sodium	$\text{Na} \rightarrow \text{Na}^+$	
Calcium	$\text{Ca} \rightarrow \text{Ca}^{2+}$	Note: These are also in decreasing order of electrode potential, or more simply the amount of electrical energy required to effect the conversion of ion to atom e.g. $\text{Cu}^{+2} \rightarrow \text{Cu}$. The series is thus of use in explaining the mechanism of electrolysis of aqueous solutions and in predicting the products of such electrolyses. (See the following pages)
Magnesium	$\text{Mg} \rightarrow \text{Mg}^{2+}$	
Aluminium	$\text{Al} \rightarrow \text{Al}^{3+}$	
Zinc	$\text{Zn} \rightarrow \text{Zn}^{2+}$	
Iron	$\text{Fe} \rightarrow \text{Fe}^{2+}$	
Lead	$\text{Pb} \rightarrow \text{Pb}^{2+}$	
Hydrogen	$\text{H} \rightarrow \text{H}^+$	
Copper	$\text{Cu} \rightarrow \text{Cu}^{2+}$	
Hydroxide	$\text{OH}^- \rightarrow [\text{OH}]$	
Silver	$\text{Ag} \rightarrow \text{Ag}^+$	
Bromide	$\text{Br}^- \rightarrow \text{Br}$	least electropositive
Chloride	$\text{Cl}^- \rightarrow \text{Cl}$	
Sulphate	$\text{SO}_4^{2-} \rightarrow [\text{SO}_4]$	

Since less energy is required to convert $\text{K} \rightarrow \text{K}^+$ than to convert $\text{Ag} \rightarrow \text{Ag}^+$, the E.C.S. gives us a fairly accurate idea of the relative reactivity of the elements and their compounds (see page 97). Thus elements at the top are much more reactive than elements at the bottom and consequently compounds of elements at the top are in general more stable than compounds of elements at the bottom.

Electrolysis

Definition *Electrolysis is the decomposition of an electrolyte (in the fused state or in solution) by the passage of an electric current.*

Since an electric current can be regarded as a stream of electrons moving in a conductor in a direction opposite to that of the conventional current, an electrolyte must be capable of conducting electricity, i.e. of transferring the electrons from cathode to anode to complete the circuit (fig. 4). Thus it must contain free ions and must therefore be an electrovalent substance in solution or in the molten (fused) state.

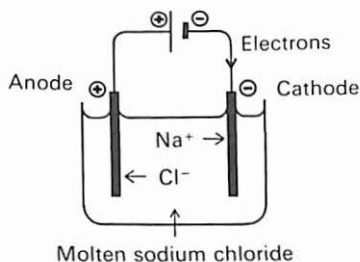


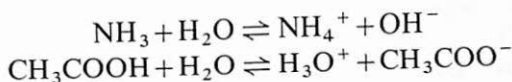
fig. 4

Purely covalent compounds such as sugar ($C_{12}H_{22}O_{11}$) or alcohol (C_2H_5OH) are not electrolytes as they do not conduct electricity at all. However there are some covalent compounds which become ionic, due to proton shifts, when dissolved in water, e.g.

Weak electrolytes

Ammonia gas

Acetic acid

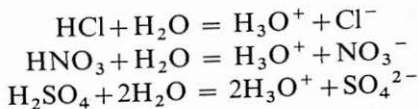


Strong electrolytes

Hydrogen chloride

Nitric acid

Sulphuric acid



[H_3O^+ the hydroxonium ion, is simply a hydrated H^+ ion ($H_2O + H^+$).] Some of these solutions are weak electrolytes as they do not ionise completely, and others which do ionise completely are called strong electrolytes (see page 22). The conductance of a strong electrolyte is greater than that of a weak electrolyte.

In a covalent solvent, such as toluene, this shift does not take place and the compound does not ionise (see hydrogen chloride, page 82).

CONDITIONS DETERMINING THE PRODUCTS OF ELECTROLYSIS

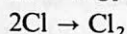
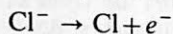
If the electrolyte is a fused salt, e.g. molten sodium chloride (fig. 4), then the process is simple.



The current (stream of electrons) creates a negative polarity in one of the electrodes (the cathode), and a positive polarity in the other (the anode). Positive ions are attracted to the cathode and negative ions to the anode.

At anode \oplus

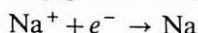
Chloride ions are discharged, i.e. they lose electrons.



The atoms so formed pair together forming chlorine gas.

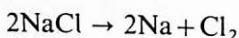
At cathode \ominus

Sodium ions are discharged, i.e. they gain electrons.

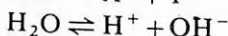
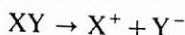


Sodium metal is formed.

Net result



If, however, the electrolyte is in aqueous solution, ions from the water complicate the situation. Consider the substance XY dissolved in water.



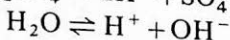
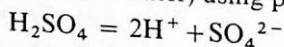
In general, if X^+ is higher than H^+ on the E.C.S. (shown on page 12), H^+ discharges preferentially, since less energy is required for $\text{H}^+ \rightarrow \text{H}$ than for $\text{X}^+ \rightarrow \text{X}$. For similar reasons, if X^+ is lower than H^+ , X^+ discharges.

If Y^- is higher than OH^- , Y^- would discharge in preference, if lower, then OH^- would discharge. Factors affecting these discharges are:

- a the concentration of the electrolyte;
- b the nature of the electrodes.

ELECTROLYSIS OF VARIOUS SYSTEMS

a Dilute sulphuric acid (acidified water) using platinum electrodes.

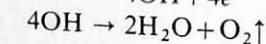
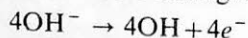


At anode \oplus

$\left. \begin{array}{l} \text{OH}^- \\ \text{SO}_4^{2-} \end{array} \right\}$ both present

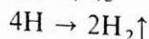
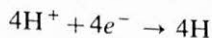
OH^- higher than SO_4^{2-} on E.C.S.

$\therefore \text{OH}^-$ is discharged.



At cathode \ominus

The only positive ion present is H^+



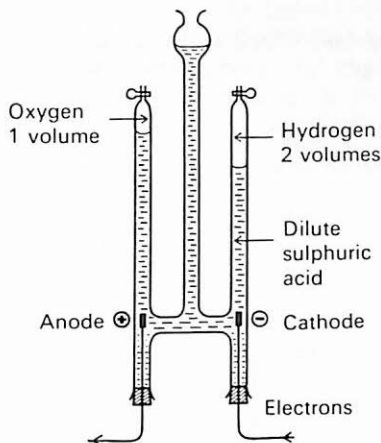


fig. 5 Hoffmann voltameter

Net result

1 volume of oxygen is formed at the anode.

2 volumes of hydrogen are formed at the cathode.

The sulphuric acid is unchanged since only H^+ and OH^- ions are removed from the system.

b Sodium chloride solution (brine) using carbon electrodes.

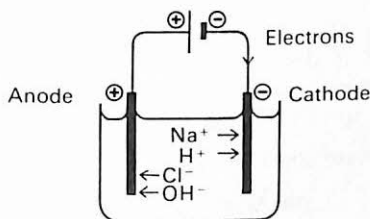
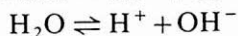


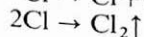
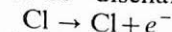
fig. 6

At anode ⊕

OH^- } both present
 Cl^- }

OH^- is higher than Cl^- on E.C.S. but the concentration of Cl^- is greater than that of OH^-

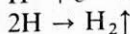
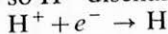
∴ Cl^- discharges.



At cathode ⊖

Na^+ } both present
 H^+ }

Na^+ is higher than H^+ so H^+ discharges.



Net result

1 volume of chlorine is formed at the anode.

1 volume of hydrogen is formed at the cathode.

Since H and Cl ions are used up, the solution is slowly converted to sodium hydroxide (Na^+ and OH^- left).

c Copper (II) sulphate solution using platinum electrodes.

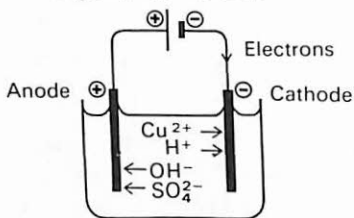
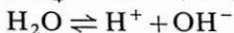
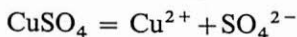
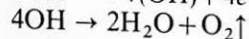
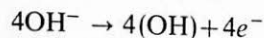


fig. 7

At anode \oplus

SO_4^{2-}
 OH^- } both present

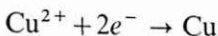
SO_4^{2-} is very stable,
so OH^- is discharged.



At cathode \ominus

Cu^{2+}
 H^+ } both present

H^+ is above Cu^{2+}
on E.C.S. $\therefore \text{Cu}^{2+}$ is preferentially discharged.



Net result

Oxygen is evolved at the anode.

Copper is deposited on the cathode.

The copper (II) sulphate solution is converted to sulphuric acid since the Cu^{2+} and OH^- ions are used up.

d Copper (II) sulphate solution using copper electrodes.

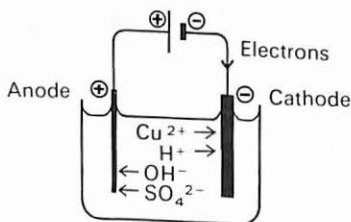
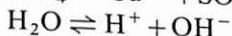
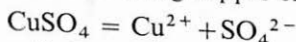
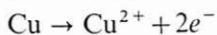


fig. 8

At anode \oplus

The conditions are the same as in (c), but this time copper atoms from the anode lose electrons and become ions.



Net result

The anode becomes smaller.

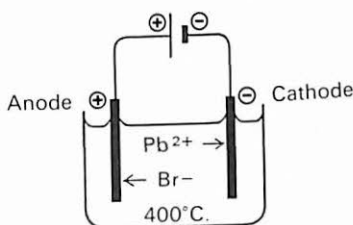
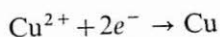
The cathode becomes larger.

The copper (II) sulphate solution remains unchanged.

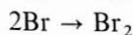
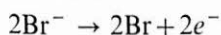
e Fused lead bromide.

At cathode \ominus

As on page 16.



At anode \oplus

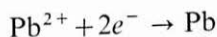


Net result

Lead is formed on the cathode.

Brown fumes of bromine are evolved at the anode.

At cathode \ominus



APPLICATIONS OF ELECTROLYSIS

Electroplating

Chromium, silver and gold plating are common processes. The metal object to be plated is made the cathode in a suitable electrolyte containing positive ions of the plating material. Important factors which influence the quality of the plating are: the temperature, the current, the concentration of the electrolyte and the cleanliness of the surface to be plated.

Extraction and purification of metals (see p. 94).

Manufacture of various gases by electrolytic processes, e.g. chlorine from the electrolysis of brine. (See p. 77)

2 Oxygen and oxides

The composition of the air

Oxygen	20%
Nitrogen	78%
Carbon dioxide	0.03%
Inert gases (argon, neon and helium)	1%
Water vapour	variable, depending on the humidity

The effect of heating elements in air

Element	Symbol	Noticeable effect	Name	Product description	Formula
Carbon	C	red/orange flame	carbon dioxide	colourless gas	CO_2
Sulphur	S	blue flame	sulphur dioxide	colourless gas	SO_2
Phosphorus	P	white flame	diphosphorus pentoxide	white smoky gas	P_2O_5
Sodium	Na	yellow flame	sodium peroxide	white solid	Na_2O_2
Magnesium	Mg	white glow	magnesium oxide	white solid	MgO
Zinc	Zn	white glow	zinc oxide	white solid	ZnO
Copper	Cu	red glow	copper (II) oxide	black solid	CuO
Iron	Fe	red glow	iron (III) oxide	blue grey solid	Fe_3O_4
Lead	Pb	melts	lead monoxide	yellow solid	PbO
Tin	Sn	melts	tin (II) oxide	white solid	SnO_2

An element gains weight when it is burnt in air, i.e. some of the air combines with the element.

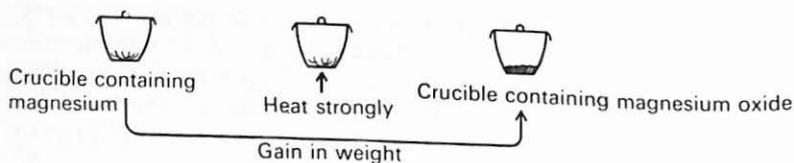


fig. 10

The portion of the air used in burning is approximately one fifth (by volume) as proved by the following experiment.

The water levels inside and outside the tube are equalised and the apparatus is left for a few days. It is then found that the water has risen up the tube to a distance of one fifth of the total length. Since the tube is uniform this means that the percentage of oxygen in the air is approximately 20%.

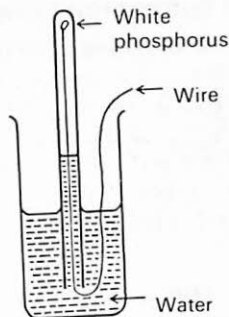
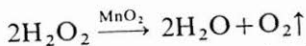


fig. 11

The laboratory preparation of oxygen

Hydrogen peroxide is decomposed rapidly at room temperature in the presence of manganese (IV) oxide to produce oxygen.



The manganese (IV) oxide acts as a *catalyst* in this section. A catalyst is a substance which alters the rate of a chemical reaction without itself undergoing any chemical change.

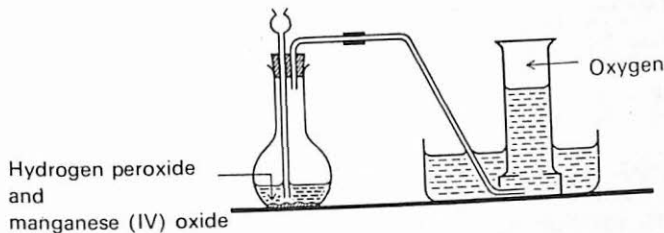
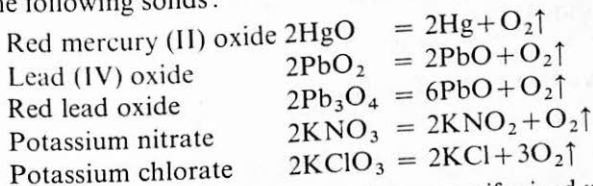


fig. 12 The preparation of oxygen

Oxygen may be produced in smaller quantities in the laboratory by heating the following solids:



Such solids are oxidising agents and are dangerous if mixed with easily oxidised materials, e.g. sulphur, carbon, or organic compounds.

The commercial preparation of oxygen

The most obvious and the cheapest source of oxygen is the air. Carbon dioxide and water are removed from air, which is then compressed and allowed to expand suddenly. This produces a cooling effect, turning the gas into a liquid. The liquid air, which is a mixture of mainly liquid nitrogen and oxygen, is fractionally distilled, yielding first nitrogen and then oxygen. The oxygen is stored and conveyed under high pressure in steel cylinders.

The uses of oxygen

Cutting and welding. Oxy-hydrogen blowpipe, 2000°C ; oxy-acetylene (see p. 37) blowpipe, 3000°C .

An aid to breathing. Oxygen at a pressure greater than normal is used in oxygen tents and cylinders in hospitals, high altitude flying or climbing, submarines and mine rescue work.

Steel production. Compressed oxygen blasts are used to reduce the carbon content and to remove various other elements present in the crude iron.

The reaction of metals and non-metals with oxygen

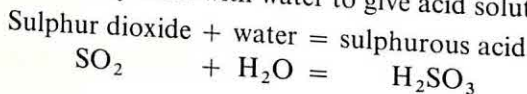
Metals	Equation	Action of water on oxide	Action of litmus	Acidic or basic
Calcium	$2\text{Ca} + \text{O}_2 = 2\text{CaO}$	$\text{CaO} + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$	blue	basic
Magnesium	$2\text{Mg} + \text{O}_2 = 2\text{MgO}$	$\text{MgO} + \text{H}_2\text{O} = \text{Mg}(\text{OH})_2$	blue	basic
Iron	$3\text{Fe} + 2\text{O}_2 = \text{Fe}_3\text{O}_4$	insoluble	—	—
Non-metals				
Carbon	$\text{C} + \text{O}_2 = \text{CO}_2$	$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$	red	acidic
Sulphur	$\text{S} + \text{O}_2 = \text{SO}_2$	$\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3$	red	acidic
Phosphorus	$4\text{P} + 5\text{O}_2 = 2\text{P}_2\text{O}_5$	$2\text{P}_2\text{O}_5 + 2\text{H}_2\text{O} = 4\text{HPO}_3$	red	acidic

The conclusion from these reactions is that metals form basic oxides, and non-metals form acidic oxides, when they react with oxygen. However, this is only a general statement since various other types of oxides may be formed.

The classification of oxides

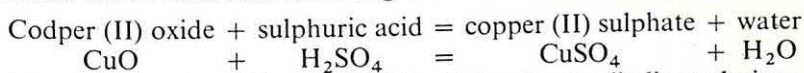
a Acidic oxides

Oxides which normally react with water to give acid solutions, e.g.

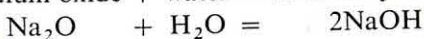
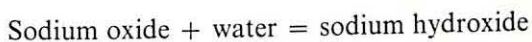


b Basic oxides

Oxides which react with acids to give a salt and water only, e.g.



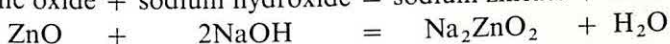
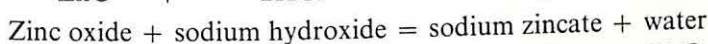
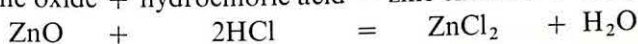
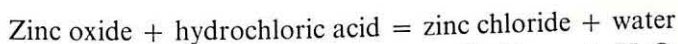
Note: Some basic oxides are soluble, giving rise to alkaline solutions, e.g.



(Sodium hydroxide is an *alkali*.)

c Amphoteric oxides

Oxides which react with both acids and bases to form salts and water, e.g.



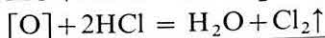
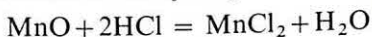
Another example is aluminium oxide which forms *aluminium chloride* and *sodium aluminate* under similar conditions.

d Higher oxides

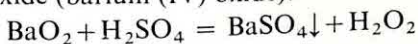
Oxides which contain more oxygen than is necessary to satisfy the valency of the other element, e.g. manganese (IV) oxide, MnO_2 .

Manganese (valency 2) gives manganese (II) oxide, MnO .

The extra oxygen shows up in the oxidising action of the oxide, for instance in its oxidation of hydrogen chloride.

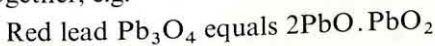


Note: Some higher oxides are known as peroxides. A peroxide is a substance which gives hydrogen peroxide when treated with an acid, e.g. barium peroxide (barium (IV) oxide).



e Compound oxides

Oxides which react as if they are made up of other simpler oxides loosely joined together, e.g.



f Neutral oxides

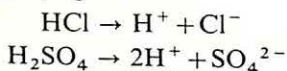
Oxides which have neither acidic nor basic nor any other definite character which would place them in a special oxide class, e.g. carbon monoxide (CO); nitrogen monoxide (NO); water (H_2O).

3 Acids, bases and salts

Acids

An acid is a substance which turns blue litmus red and which contains hydrogen replaceable by a metal.

A more modern definition is that an acid is a substance which, when in solution, produces H^+ ions, e.g.

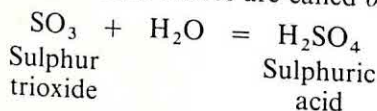


Acids may be classified under two major headings.

a **Mineral acids**, derived from substances found in the earth.

Acid	Formula	Source	Formula
Hydrochloric	HCl	common salt	NaCl
Sulphuric	H ₂ SO ₄	sulphur	S
Nitric	HNO ₃	Chilean saltpetre	NaNO ₃
Carbonic	H ₂ CO ₃	limestone	CaCO ₃
Sulphurous	H ₂ SO ₃	sulphur	S

Those mineral acids made from oxides are called *oxy acids*, e.g.



b **Organic acids**, derived from plant and animal sources.

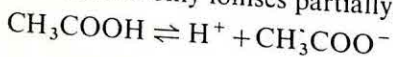
Acid	Formula	Occurrence
Acetic	CH ₃ COOH	vinegar
Citric	C ₃ H ₅ O(COOH) ₃	lemon juice
Tartaric	C ₂ H ₄ O ₂ (COOH) ₂	cream of tartar

Acids may be *strong* or *weak* depending on whether or not they ionise completely in aqueous solution, e.g.

Hydrochloric acid is a *strong* acid as it ionises completely.



Acetic acid is a *weak* acid as it only ionises partially.



Bases

A base is a substance which reacts with an acid to give a salt and water only, e.g. copper (II) oxide.



In addition to basic oxides, other examples of bases are metal hydroxides, e.g. lead (II) hydroxide $\text{Pb}(\text{OH})_2$ and zinc hydroxide $\text{Zn}(\text{OH})_2$. Some bases form alkaline solutions with water.

ALKALIS

An alkali is a soluble hydroxide which turns red litmus blue and produces OH^- ions in solution, e.g. sodium hydroxide



Alkalis fall into several different categories.

a Caustic as opposed to mild

Caustic: sodium hydroxide—caustic soda NaOH
potassium hydroxide—caustic potash KOH

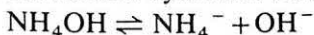
Mild: calcium hydroxide—slaked lime $\text{Ca}(\text{OH})_2$
magnesium hydroxide—milk of magnesia $\text{Mg}(\text{OH})_2$

b Strong and weak — as with acids

Strong: sodium hydroxide ionises completely



Weak: ammonium hydroxide ionises only partially



Salts

A salt is a substance formed when the replaceable hydrogen of an acid is wholly or partially replaced by a metal or other positive radical.

The salt gets part of its name from the acid and part from the metal, e.g.

Salts of sulphuric acid are sulphates.

Salts of hydrochloric acid are chlorides.

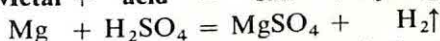
Salts of nitric acid are nitrates.

Salts of acetic acid are acetates.

Thus the salt formed from magnesium and sulphuric acid is called magnesium sulphate, MgSO_4 .

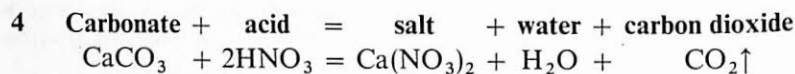
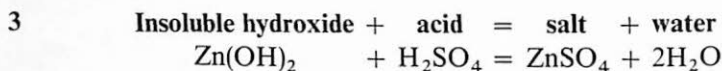
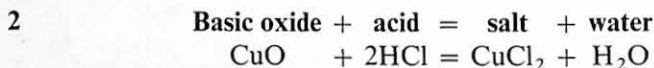
PREPARATION OF SALTS

1 $\text{Metal} + \text{acid} = \text{salt} + \text{hydrogen}$



This applies mainly to metals above hydrogen in the electro-chemical series and to dilute acids.





Experimental procedure for making salts by methods 1, 2, 3 and 4

a Pour 30 ml of the dilute acid into a beaker.

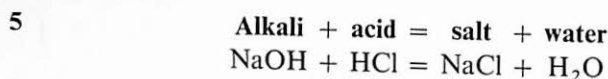
b Add the solid (metal, oxide, hydroxide or carbonate) in small quantities, heating and stirring until no more dissolves.

c Filter into an evaporating basin.

d Concentrate the filtrate by evaporation until a drop, when suspended on the end of a glass rod, shows the formation of crystals, and allow to cool.

e Carefully evaporate the resulting solution to dryness, if the solution is normally anhydrous, or concentrate it and allow it to crystallise if it contains water of crystallisation.

Note: Insoluble salts such as lead II sulphate (PbSO_4) cannot be made by this method.



Experimental procedure for method 5

a Pipette 25 ml of alkaline solution into a conical flask.

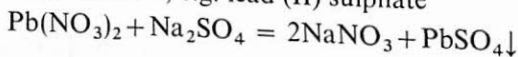
b Add 10 drops of litmus which turns the solution blue.

c Add the acid from a burette until the colour changes to red and note the volume added.

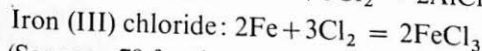
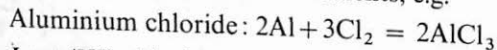
d Repeat (a), (b) and (c) omitting the litmus.

e Carefully evaporate the resulting solution to dryness or concentrate it and allow it to crystallise.

6 Double decomposition (precipitation) This is the recognised method for making insoluble salts, e.g. lead (II) sulphate



7 Direct combination For various reasons the methods using acids are not suitable for the preparation of some salts, which must therefore be prepared from their elements, e.g.



(See page 79 for the action of chlorine on metals.)

4 Hydrogen and water

Hydrogen

Hydrogen is a colourless, odourless gas which is very much lighter than air and almost insoluble in water. It does not occur freely to any marked degree but occurs in the combined state in a very large variety of compounds e.g. water H_2O ; hydrocarbons such as methane CH_4 ; carbohydrates such as sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$.

PREPARATION OF HYDROGEN

1 Metals and water

The first few metals in the electrochemical series react with decreasing reactivity with water to produce hydrogen (see page 25).

a Sodium and potassium These metals react very vigorously with cold water. They float, melt to form a round ball, and dart at random over the surface of the water, being propelled by the hydrogen given off. In

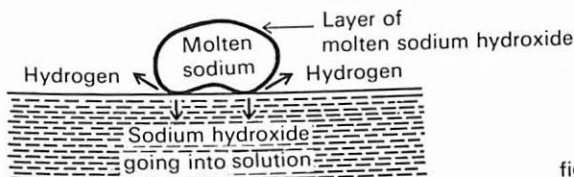
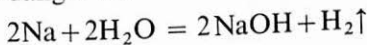
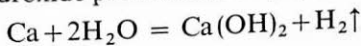


fig. 13

the case of potassium, the hydrogen burns with a lilac flame. Note that the reaction can be dangerous.



b Calcium Calcium sinks in cold water and reacts to give off bubbles of hydrogen. Eventually a white suspension is formed due to the fact that the calcium hydroxide produced is only sparingly soluble in water.



c Magnesium Magnesium, when burning, reacts with hot water or steam to produce the hydroxide and hydrogen.

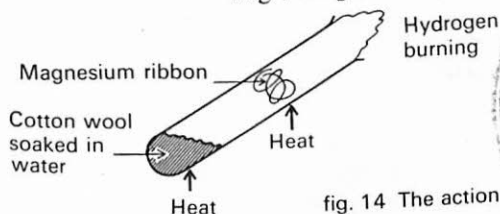
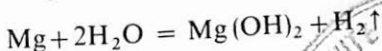


fig. 14 The action of steam on burning magnesium



d *Iron* Iron when red hot reacts reversibly with steam.

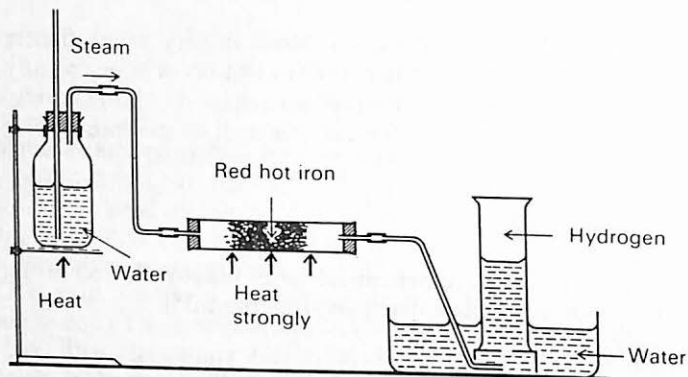
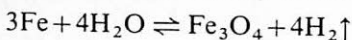


fig. 15 The action of steam on red hot iron

2 Metals and acids

All metals above hydrogen in the electrochemical series (page 12) theoretically react with dilute, non-oxidising acids to produce hydrogen.

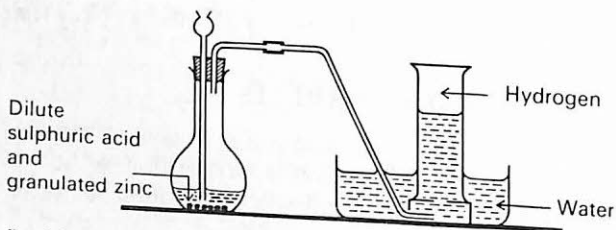
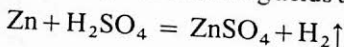
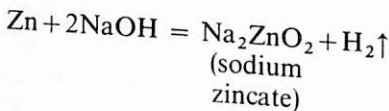


fig. 16 The preparation of hydrogen

Note: Lead and aluminium are unsuitable for this preparation as they react too slowly. Sodium, potassium and calcium would give explosively violent reactions.

3 Metals and alkalis

Zinc and aluminium react with caustic alkalis to form a salt and hydrogen.



USES OF HYDROGEN

In fuels

Hydrogen alone would be too dangerous to use as a fuel, but it is widely used in conjunction with other gases.

Water gas: carbon monoxide + hydrogen (page 42).

Coal gas: methane + hydrogen + carbon monoxide (page 42).

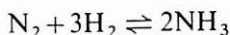
Oxy-hydrogen flame for cutting and welding.

Hardening of oils

Peanut and coconut oils are 'hardened' by being combined with hydrogen in the presence of a nickel catalyst. Thus they are converted into edible solid fats.

Haber process

Ammonia is produced on a large scale by passing a mixture of 1 volume of nitrogen and 3 volumes of hydrogen over an iron oxide catalyst at a high temperature and a high pressure (page 84).



Water

Water, H_2O , is a simple oxide of hydrogen and is produced together with other products and energy when hydrogen and hydrogen containing substances are burned in air or oxygen, e.g

Methane: $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O} + \text{heat}$

Alcohol: $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 = 2\text{CO}_2 + 3\text{H}_2\text{O} + \text{heat}$

HYDROGEN BURNS IN AIR TO FORM WATER

This is a very dangerous reaction. The hydrogen should be collected in test-tubes and a light applied. If it 'pops', it contains air. It should not be lit at the jet until a test-tube sample burns quietly with a blue flame.

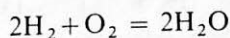
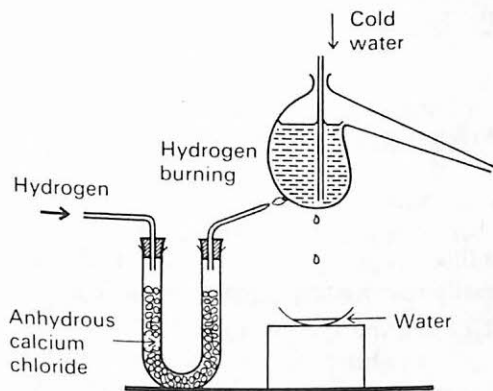
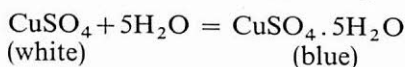


fig. 17 Hydrogen burning in air to form water

The colourless liquid produced may be tested with anhydrous copper II sulphate, which turns from white to blue, proving that water is present.



Pure water freezes at 0°C at a pressure of 760 mm of mercury.
Pure water boils at 100°C at a pressure of 760 mm of mercury.

REDUCTION OF METAL OXIDES USING HYDROGEN

Hydrogen can 'remove' the oxygen from certain metal oxides. Water is formed and the oxide is reduced to the metal, e.g.

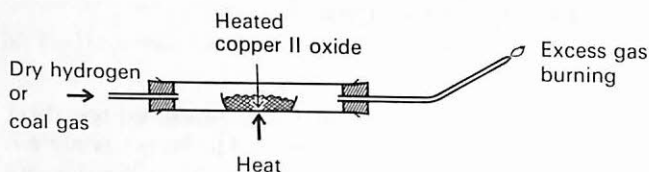
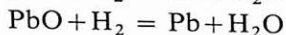
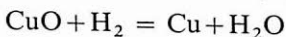
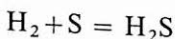


fig. 18 Reduction of heated copper (II) oxide

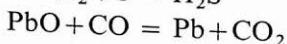
This process is known as *reduction* which can be regarded as the opposite of *oxidation*.

Reduction

Addition of hydrogen, e.g.

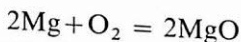


Removal of oxygen, e.g.

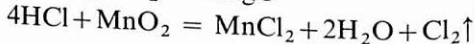


Oxidation

Addition of oxygen, e.g.

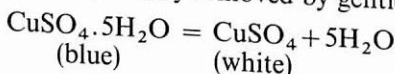


Removal of hydrogen, e.g.



WATER OF CRYSTALLISATION

This refers to the fixed number of water molecules which join with certain salts when they crystallise from aqueous solution. It is only loosely attached and can be easily removed by gentle heating, e.g.



The colourless liquid which collects in the cooled test-tube can be tested as before and proved to be water.

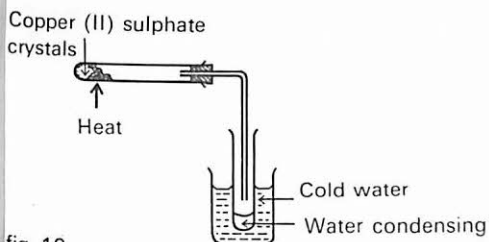


fig. 19

The percentage of water of crystallisation can be determined practically.

- 1 Weigh a crucible and lid (x grams).
- 2 Weigh a crucible and lid and some crystals of a hydrated salt (y grams).
- 3 Heat for fifteen minutes.
- 4 Cool and weigh again.
- 5 Heat, cool and weigh again (z grams).

Weight of hydrated salt = $(y - x)$ grams

Weight of water = $(y - z)$ grams

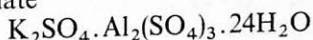
Percentage of water of crystallisation = $\frac{(y - z)}{(y - x)} \times 100\%$

Some substances which contain water of crystallisation are:

Epsom salts – magnesium sulphate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Washing soda – sodium carbonate $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

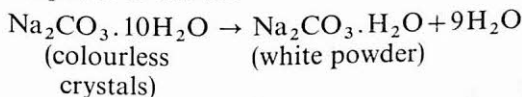
Potash alum – potassium aluminium sulphate



EFFLORESCENCE

This term is used to describe a process by which water of crystallisation is lost when some substances are exposed to the air, e.g.

Colourless crystals of washing soda become covered with a white powder when exposed to the air.



Such substances are said to be *efflorescent*.

DELIQUESCENT

This describes the process whereby some substances absorb moisture from the air and dissolve in the absorbed moisture, e.g.

Anhydrous calcium chloride, CaCl_2

Sodium hydroxide, NaOH

Such substances are said to be *deliquescent*.

HYGROSCOPY

A hygroscopic substance is one which simply absorbs moisture from the air without dissolving, e.g. glass, paper, and copper oxide. Such substances are said to be *hygroscopic*.

DRYING AGENTS

It is frequently necessary to remove traces of moisture from chemical substances. The following methods are commonly used.

a Solids

The solid (x) to be dried is placed in a container in the top compartment of a *desiccator* in the bottom of which is a drying agent (y).

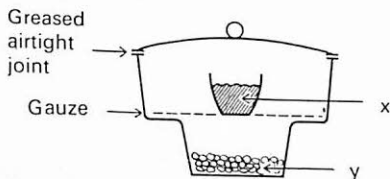


fig. 20 A desiccator

Suitable drying agents for use in a desiccator are: anhydrous calcium chloride; silica gel.

b Liquids

The liquid is left for a few hours in contact with the drying agent, e.g.

Anhydrous calcium chloride is used to dry ethylene dibromide.
Sodium metal is used to dry ether.

c Gases

i The gas is passed through a U-tube packed loosely with the drying agent (anhydrous calcium chloride; soda lime).

See the special case of ammonia, page 83.

ii The gas is bubbled through concentrated sulphuric acid in a washing bottle or Dreschel bottle.

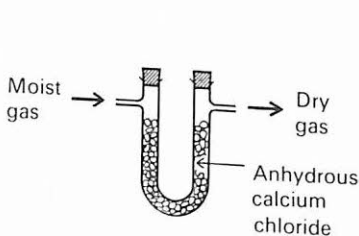


fig. 21 A U-tube

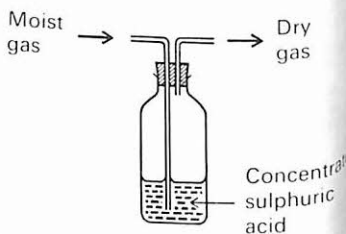


fig. 22 A gas washing (drying) bottle or a Dreschel bottle

Note: The drying agent in all cases must not react with the substance being dried.

5 Carbon and its compounds

Carbon occurs

a In the free state as diamond and graphite

b In the combined state as :

Limestone, chalk, marble (all CaCO_3) and other carbonates.

Carbon dioxide of the air.

Petroleum products.

Coal.

Organic compounds in plants and animals, e.g. carbohydrates, vitamins.

Allotropy

Carbon can exist in two different physical forms, both of which have the same chemical properties. This phenomenon is known as *allotropy* and the different forms as *allotropes*.

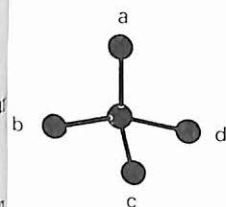


fig. 23 Diamond

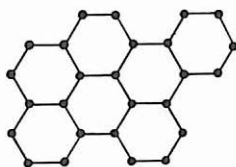


fig. 24 Graphite

DIAMOND

The atoms of carbon are arranged in a regular tetrahedral structure as shown. Each of the atoms *a*, *b*, *c*, and *d* are attached to three other atoms etc., thus producing a rigid three-dimensional structure.

Diamond is very hard. It is used for drill tips and glass-cutters, and has a brilliant lustre which makes it very attractive and in great demand for jewellery.

GRAPHITE

The atoms are arranged in layers of hexagons with the fourth valency bonds of the atoms holding the layers loosely together. Graphite is a black, greasy solid. It is the only non-metal which conducts electricity and is also used as a lubricant and, mixed with clay, as the 'lead' in pencils.

Several other forms of carbon also have a graphite type structure.

Wood charcoal

Preparation : wood is heated strongly in the absence of air.

Uses : as a fuel and a gas absorbent.

Animal charcoal

Preparation: bones are heated in the absence of air; animal charcoal therefore contains calcium phosphate as well as carbon.

Uses: to decolourise liquids, e.g. in the manufacture of white sugar from brown sugar solution.

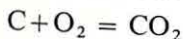
Lampblack

Preparation: a hydrocarbon, e.g. kerosene, is burned in an extremely limited supply of air.

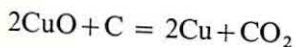
Uses: as a pigment for Indian ink and printers' ink.

Properties of carbon

a All forms burn in oxygen to form carbon dioxide.



b Carbon is a reducing agent, i.e. it removes oxygen from some oxides leaving the metal.



Proof

i Test copper (II) oxide with concentrated nitric acid. Blue solution no gas.

ii Heat copper (II) oxide/carbon mixture strongly. The gas turns lime water milky.

Copper (II) oxide
+ carbon

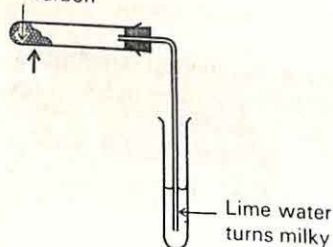


fig. 25

iii Test cooled residue with concentrated nitric acid. Blue solution brown gas. Copper is present. (See page 39 for an explanation.)

Carbon dioxide

Carbon dioxide plays a vital part in several natural processes and is essential for the continuance of life on this planet, the balance in nature being maintained by a cycle as shown on the next page.

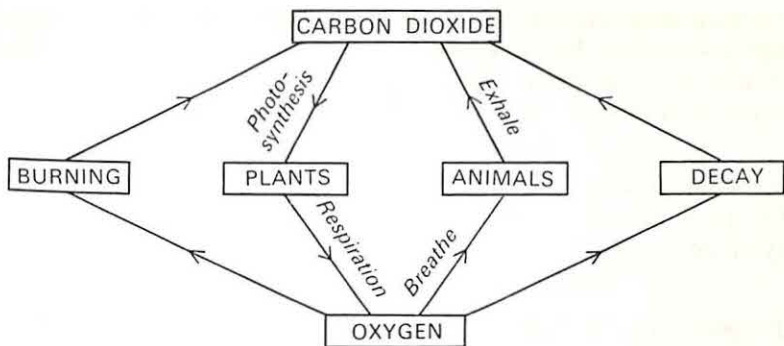


fig. 26 The carbon cycle in nature

PREPARATION OF CARBON DIOXIDE

Carbon dioxide is normally prepared in the laboratory by adding dilute hydrochloric acid to marble chips.

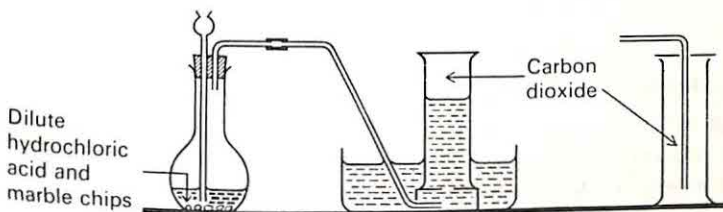
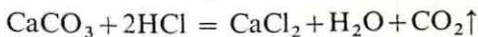


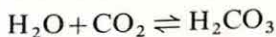
fig. 27 The preparation of carbon dioxide

Note: Sulphuric acid may *not* be used as it forms an insoluble coating of calcium sulphate around each particle of marble, thus stopping the reaction.

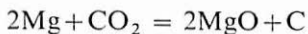
The gas may be collected over water as it is only sparingly soluble, or by downward delivery as it is denser than air.

PROPERTIES OF CARBON DIOXIDE

- 1 Colourless, odourless gas, sparingly soluble in water and denser than air.
- 2 Reacts with water to form carbonic acid.

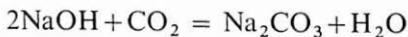


- 3 Reaction with magnesium. Carbon dioxide does not normally support combustion, but a fiercely burning substance will continue to burn in it. Burning magnesium can decompose carbon dioxide, forming magnesium oxide and carbon.

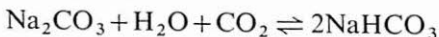


- 4 Action on alkalis.

i Carbon dioxide is absorbed by both potassium and sodium hydroxides, forming the soluble carbonates:



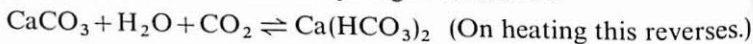
and subsequently the hydrogen carbonates:



ii Carbon dioxide turns lime water (calcium hydroxide solution) milky. This is due to the formation of insoluble calcium carbonate and serves as a test for carbon dioxide.



On continued passing, the solution turns clear again due to the formation of soluble calcium hydrogen carbonate.



USES OF CARBON DIOXIDE

1 Refrigeration

Solid carbon dioxide (dry ice) is at a temperature of -78°C and is used to keep foodstuffs, such as ice cream, cold in transit.

2 Aerated waters

Carbon dioxide is dissolved under pressure in water to make soda water and in flavoured drinks to make so-called 'mineral waters'. On opening sealed bottles of such beverages, the gas escapes, producing effervescence.

3 Fire extinguishers

There are many types, all of which produce, in some way, a stream of carbon dioxide or carbon dioxide mixed with an aqueous solution. A dense blanket of carbon dioxide forms over a fire, so extinguishing it by preventing any further intake of air. The more modern types of extinguishers produce a stream of very cold particles of solid carbon dioxide.

4 Solvay process

In this process carbon dioxide, ammonia, salt and water are combined to produce sodium hydrogen carbonate and sodium carbonate.

Carbonates and hydrogen carbonates

These are salts of the weak acid carbonic acid H_2CO_3 .

Formula	Colour	Solubility	Action of heat	Action of acid
Na_2CO_3	white	soluble	no action	$\text{Na}_2\text{CO}_3 + 2\text{HCl} = 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2\uparrow$
K_2CO_3	white	soluble	no action	$\text{K}_2\text{CO}_3 + 2\text{HCl} = 2\text{KCl} + \text{H}_2\text{O} + \text{CO}_2$
CaCO_3	white	insoluble	$\text{CaCO}_3 = \text{CaO} + \text{CO}_2\uparrow$	$\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2\uparrow$
MgCO_3	white	insoluble	$\text{MgCO}_3 = \text{MgO} + \text{CO}_2\uparrow$	$\text{MgCO}_3 + \text{H}_2\text{SO}_4 = \text{MgSO}_4 + \text{H}_2\text{O} + \text{CO}_2\uparrow$
ZnCO_3	white	insoluble	$\text{ZnCO}_3 = \text{ZnO} + \text{CO}_2\uparrow$	$\text{ZnCO}_3 + 2\text{HCl} = \text{ZnCl}_2 + \text{H}_2\text{O} + \text{CO}_2\uparrow$
PbCO_3	white	insoluble	$\text{PbCO}_3 = \text{PbO} + \text{CO}_2\uparrow$	$\text{PbCO}_3 + 2\text{HNO}_3 = \text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{O} + \text{CO}_2\uparrow$
CuCO_3	green	insoluble	$\text{CuCO}_3 = \text{CuO} + \text{CO}_2\uparrow$	$\text{CuCO}_3 + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O} + \text{CO}_2\uparrow$
NaHCO_3	white	soluble	$2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2\uparrow$	$\text{NaHCO}_3 + \text{HCl} = \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2\uparrow$
KHCO_3	white	soluble	$2\text{KHCO}_3 = \text{K}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2\uparrow$	$\text{KHCO}_3 + \text{HCl} = \text{KCl} + \text{H}_2\text{O} + \text{CO}_2\uparrow$

Note:

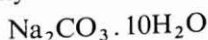
- Sodium and potassium carbonates are exceptions, except in their action with acids.
- Their hydrogen carbonates are the only stable hydrogen carbonates.

TEST FOR CARBONATE OR HYDROGEN CARBONATE

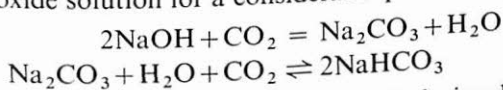
The evolution of carbon dioxide on addition of dilute hydrochloric acid serves as a test (see table above).

WASHING SODA AND BAKING SODA

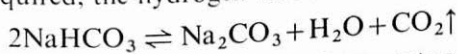
Washing soda is the decahydrate of sodium carbonate, i.e.



It is used as a harsh detergent for washing floors, milk bottles, etc. Baking soda is sodium hydrogen carbonate (NaHCO_3). It is added in small quantities to cake and bread mixtures, and gives off carbon dioxide when these are heated in the oven, thus making the bread rise. These substances can be prepared by passing carbon dioxide into sodium hydroxide solution for a considerable period of time.



The sodium hydrogen carbonate, being relatively insoluble, precipitates from the solution and can be filtered off and dried. If sodium carbonate is required, the hydrogen carbonate is heated.



The carbonate can be produced in the anhydrous state or can be allowed to crystallise as washing soda from an aqueous solution.

To distinguish between them

Heat and test the gas evolved with lime water. The hydrogen carbonate (see above) evolves carbon dioxide while the carbonate does not.

CALCIUM CARBONATE, CaCO_3

This substance is found naturally in many different physical forms, the

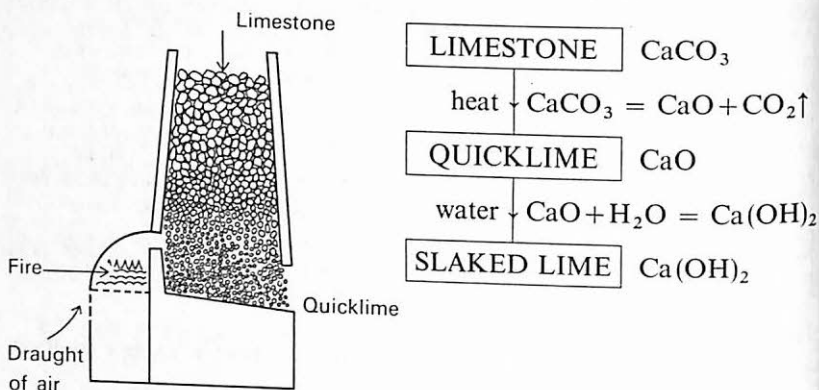


fig. 28 A lime kiln

most common being chalk, limestone and marble. Two important and familiar substances can be made from it by simple chemical processes.

USES OF LIMESTONE AND ITS PRODUCTS

a To make limewater, which is used in the laboratory as a test for carbon dioxide. Water is added slowly to quicklime which appears to absorb enormous quantities then suddenly decomposes from a hard lump to a soft powder with evolution of heat. This soft powder is slaked lime and is sparingly soluble in water.

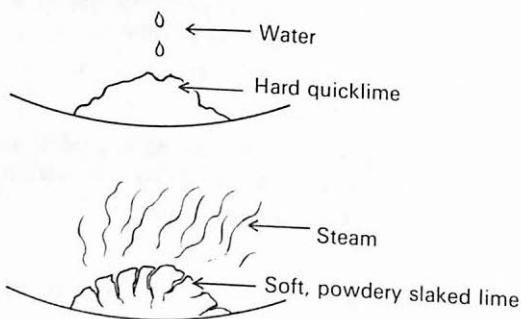
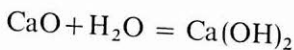
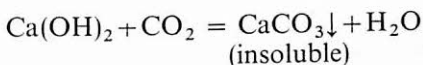


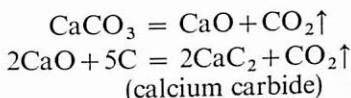
fig. 29 The slaking of quicklime

b As a mild alkali to combat 'sourness' or acidity in soil.

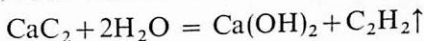
c In the manufacture of cement and mortar. Calcium hydroxide, when mixed with water and sand, constitutes mortar which loses water and sets to a hard mass. Prolonged exposure to air results in a slow reaction with carbon dioxide.



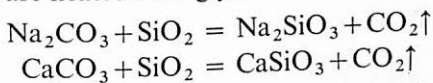
d In the manufacture of calcium carbide. Either limestone or quicklime is heated with coke in a furnace.



Calcium carbide, when treated with water, yields acetylene gas.



e In the manufacture of glass. Calcium carbonate, sodium carbonate and silica, SiO_2 , are heated strongly in a furnace.



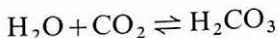
A simple form of glass is a mixture of sodium silicate and calcium silicate.

HARD WATER

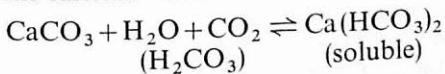
Calcium carbonate in rock formations gives rise to hard water and certain other side effects.

Causes of hardness

a Carbon dioxide of the air dissolves in rain, producing *very* dilute carbonic acid.



b This then attacks calcium carbonate.

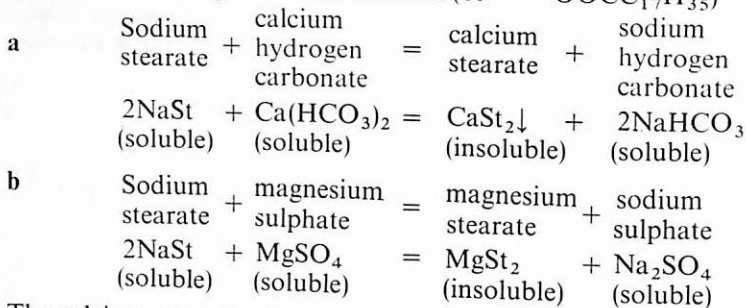


The presence of small traces of soluble calcium hydrogen carbonate causes *temporary hardness* of the water.

Another form of hardness – *permanent hardness* – is caused by small traces of other calcium and magnesium salts, e.g. their chlorides and sulphates. The effect of both types of hardness on soap is the same. Soap is a mixture of the sodium salts of some high molecular weight organic acids, e.g.

Sodium stearate, from beef tallow;
Sodium palmitate, from palm oil;
Sodium oleate, from olive oil.

Consider for example sodium stearate. ($\text{St} = -\text{OOC}_{17}\text{H}_{35}$)

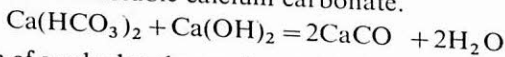


The calcium or magnesium stearate forms a scum, and until all of the Ca^{2+} or Mg^{2+} ions are removed from the water and precipitated as scum, the soap does not lather, is ineffective, and is wasted.

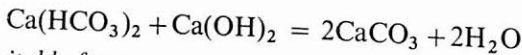
Removal of hardness

a *Methods suitable for temporary hardness only.*

i Boiling. This produces a reversal of the reaction in which calcium hydrogen carbonate is formed and all the Ca^{2+} ions are removed from solution as insoluble calcium carbonate.



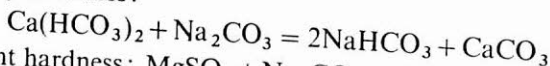
ii Addition of a calculated quantity of slaked lime. This has the same effect as (i).



b *Methods suitable for temporary and permanent hardness.*

i Addition of washing soda. Once again the Ca^{2+} or Mg^{2+} ions are removed from solution and precipitated as insoluble carbonates.

Temporary hardness:



Permanent hardness: $\text{MgSO}_4 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{SO}_4 + \text{MgCO}_3$

ii The Permutit process. This involves the passage of the hard water through an ion exchange resin, one of the simplest of which is *Permutit* (sodium aluminium silicate). Substances of this type exchange one type of ion in solution for another; in this case the exchange is Na^+ for Ca^{2+} , thus taking the hardness out of the water.

Side effects of hardness

a Formation of kettle 'fur' and boiler scale. This is simply the deposit of calcium carbonate and calcium sulphate, produced by boiling hard water. This causes inconvenience and often danger if hot water pipes become completely blocked.

b Formation of stalactites and stalagmites. Calcium hydrogen carbonate is unstable and decomposes to calcium carbonate (limestone) when it evaporates during the process of dripping from the roofs of

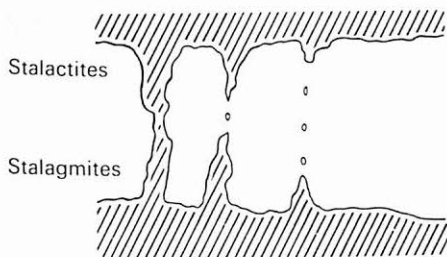


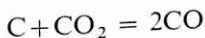
fig. 30

caves in limestone areas. A deposit of hard insoluble limestone is formed on the floor and the ceiling of the cave. These are named as indicated and sometimes join together forming pillars. They may be coloured by impurities in the limestone.

Carbon monoxide (CO)

PREPARATION OF CARBON MONOXIDE

This gaseous substance may be prepared by passing carbon dioxide through red hot carbon.



The residual gas is washed in sodium hydroxide solution which absorbs any unchanged carbon dioxide by reacting with it.

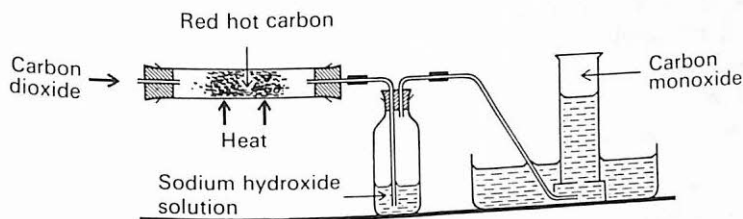
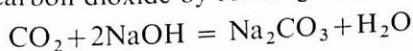
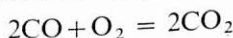


fig. 31 The preparation of carbon monoxide

PROPERTIES OF CARBON MONOXIDE

- a Colourless, odourless gas.
- b Less dense than air.
- c Insoluble in water.
- d Burns in air to form carbon dioxide.



e Is a reducing agent. Carbon monoxide can remove oxygen from some heated metal oxides, reducing them to the metal, e.g.

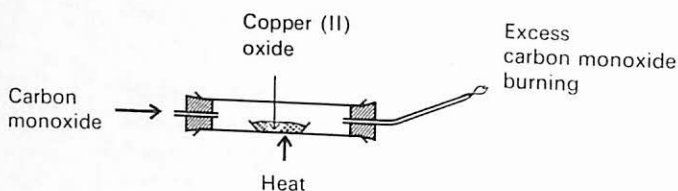
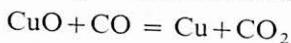


fig. 32 The reduction of hot copper (II) oxide

f Very poisonous. Normally the haemoglobin in the blood reacts with the oxygen breathed in, forming oxyhaemoglobin which circulates around the body releasing oxygen where required. If carbon monoxide is inhaled it reacts to form carboxyhaemoglobin, which is quite stable, so preventing the blood affected from absorbing oxygen. If a sufficient quantity of carbon monoxide is inhaled the person affected will die of lack of oxygen.

SOURCES OF CARBON MONOXIDE IN EVERYDAY LIFE

Carbon monoxide is formed when carbon-containing substances are burned in a limited supply of air. In a plentiful supply the product is carbon dioxide.

a Petrol (octane C_8H_{18} is the main ingredient)

Limited air supply: $\text{C}_8\text{H}_{18} + 17[\text{O}] = 8\text{CO} + 9\text{H}_2\text{O}$

Plentiful air supply: $\text{C}_8\text{H}_{18} + 25[\text{O}] = 8\text{CO}_2 + 9\text{H}_2\text{O}$

The air supply inside a car engine is limited, so the exhaust gases contain carbon monoxide and should not be inhaled.

Note: Never start a car engine in an enclosed space.

b Methane, CH_4 , a gas present in coal mines and known as firedamp.

Limited air supply: $\text{CH}_4 + 3[\text{O}] = \text{CO} + 2\text{H}_2\text{O}$

Plentiful air supply: $\text{CH}_4 + 4[\text{O}] = \text{CO}_2 + 2\text{H}_2\text{O}$

Thus when an explosion occurs in a coal mine, where there is a limited supply of air, one of the products is carbon monoxide (afterdamp) which causes considerable loss of life.

c Coke An unventilated coke fire may produce a supply of unburnt carbon monoxide. If the fire is badly ventilated, stage C cannot take place and unburnt carbon monoxide is allowed to permeate into the room causing possible poisoning.

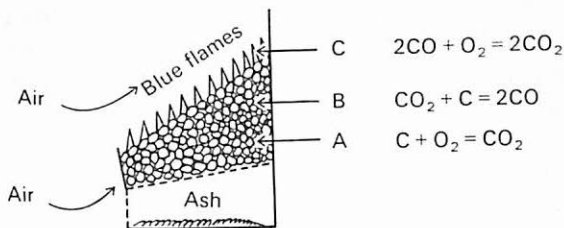


fig. 33 A coke fire

Fuels

A fuel is a substance which burns to produce energy (usually heat). Carbon, its mixtures with other substances, and many of its compounds, are efficient fuels.

SOLID FUELS

Various natural products, resulting from the decay of vegetable matter and its subsequent prolonged compression in the earth, are of use as fuels due to their high carbon content, e.g.

Anthracite

Coal

Lignite (brown coal)

Peat

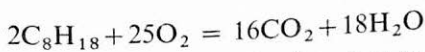
These are in decreasing order of hardness, carbon content, and therefore of thermal efficiency.

Such fuels contain many impurities resulting in a variety of waste products which produce smoke and *smog* (a mixture of smoke and fog). These contain such poisonous substances as hydrogen sulphide and sulphur dioxide and cause many deaths in industrial areas. There are campaigns for 'smokeless zones' and smokeless fuels in large cities in many parts of the world.

LIQUID FUELS

These include petroleum products such as petrol (gasoline), paraffin oil (kerosene) and diesel oil, which are formed in the earth by the decay and compression of animal remains.

They burn in a plentiful supply of air to form carbon dioxide and water and produce heat energy at the same time. Such reactions are said to be exothermic, e.g. the burning of *octane*, the main constituent of high grade petrol.



Such fuels are used in petrol engines, diesel engines and jet engines, and to fire boilers for various industrial uses.

Coal gas

This is made by heating coal in retorts in the absence of air. It may be carried out in the laboratory using simple apparatus as shown.

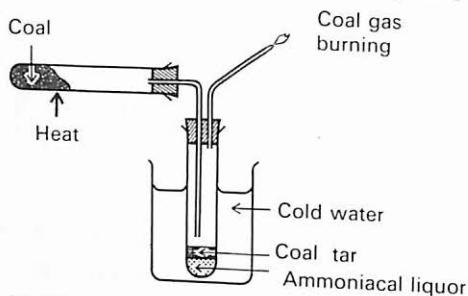
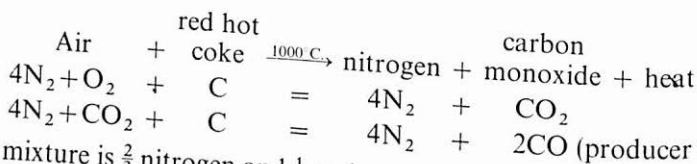


fig. 34

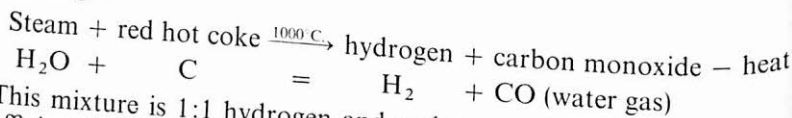
The products are as follows :

Coal (heated)	Coal gas	hydrogen 50% methane 30% carbon monoxide 10%	→ used (when purified) as a domestic and industrial fuel.
	Coal tar	benzene phenol naphthalene pitch, etc.	→ used to manufacture a variety of drugs, dyes, plastics, explosives, insecticides, etc. (organic compounds).
	Ammoniacal ammonia liquor		→ converted into ammonium salts which are used as fertilisers.
	Coke	carbon	→ a very efficient solid fuel.

For domestic use, coal gas is carefully purified to remove such substances as hydrogen sulphide and sulphur dioxide.

Producer gas

This mixture is $\frac{2}{3}$ nitrogen and $\frac{1}{3}$ carbon monoxide and is therefore not a very efficient fuel.

Water gas

This mixture is 1:1 hydrogen and carbon monoxide, and is quite an efficient fuel since both the products burn.

Producer gas and water gas are usually made together, since the heat produced in the first reaction makes up for the heat absorbed in the second, thus maintaining the reaction temperature of 1000°C . The mixture is used as a fuel to heat the coal in gas-works; and water gas is sometimes added to domestic coal gas supplies to boost them during high consumption periods.

6 Organic chemistry

This is the chemistry of carbon compounds, and its scope is vast due to the fact that carbon atoms can join together forming straight and branched chains of indefinite length and also ring structures, e.g.

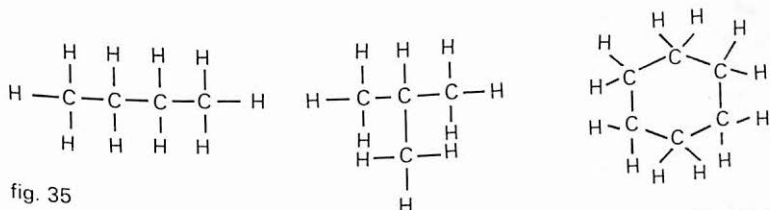


fig. 35

The four covalent bonds around each carbon atom are directed (in space) to the corners of a regular tetrahedron (fig. 36) and the four positions *a*, *b*, *c* and *d*, are occupied by carbon atoms or atoms of elements which form covalent linkages with carbon. (e.g. H, O, N, Cl, Br, I)

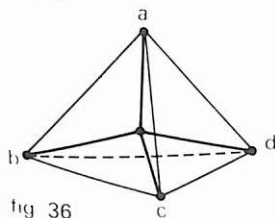


fig 36

It is seen therefore that the structures on paper above do not give a true picture of the shape of the molecules, which can best be visualised by using atomic models.

Organic compounds may be naturally occurring, as the name 'organic' suggests, comprising products from coal tar and petroleum, and carbohydrates, proteins and vitamins from animal and plant sources. They may also be synthetic (man-made), comprising a vast range of compounds such as dyes, drugs, plastics, fibres, insecticides and explosives.

Homologous series

Organic compounds are classified according to their molecular structure and each class of compounds is known as a *homologous series* which is a series of compounds of increasing molecular weight possessing similar groupings of atoms.

GENERAL PROPERTIES OF HOMOLOGOUS SERIES

a All members of the series can be represented by a general formula, e.g. $C_nH_{2n+1}OH$ represents all primary alcohols. If $n = 1$ the formula becomes CH_3OH – methyl alcohol.

b The series shows a distinct gradation in physical properties. As the molecular weight increases (i.e. as n increases) the specific gravities, melting points and boiling points of the substances increase, e.g. methane (CH_4), the first member of the paraffin series, is a light gas but the compound $C_{17}H_{36}$ in the same series is a solid.

c All the members of the series are chemically similar. This is true with limitations as there is also a slight gradation in chemical properties. It is an extremely useful fact as the chemical properties of a typical member of a homologous series represent the properties of the other members.

Note: The first member of each series is seldom typical.
The following are four of the simpler homologous series.

Paraffins (Alkanes)

These are the simplest type of hydrocarbon – compounds containing only hydrogen and carbon.

General formula: C_nH_{2n+2}

	Molecular formula	Structural formula	Molecular weight
Methane	CH_4	<pre> H H-C-H H</pre>	16
Ethane	C_2H_6	<pre> H H H-C-C-H H H</pre>	30
Propane	C_3H_8	<pre> H H H H-C-C-C-H H H H</pre>	44

	Molecular formula	Structural formula		Molecular weight
Butane	C_4H_{10}	<pre> H H H H H — C — C — C — C — H H H H H </pre> <p><i>n</i>-butane</p>	<pre> H H H H — C — C — C — H H C — H H </pre> <p>iso-butane</p>	58

Note:

a There is a constant increment of molecular weight between consecutive members of the series. $\left(\begin{array}{c} \text{H} \\ \diagup \text{C} \diagdown \\ \text{H} \end{array} = 14 \right)$

b *n*-butane (*n* = normal) and iso-butane are isomers, i.e. compounds with same molecular formulae and different structural formulae. The paraffins occur in coal mines, as natural gas and in marshes and swamps as a product of the decay of vegetation.

Preparation of methane

A mixture of anhydrous sodium acetate and soda lime (main constituent sodium hydroxide) is heated strongly and the gas collected over water.

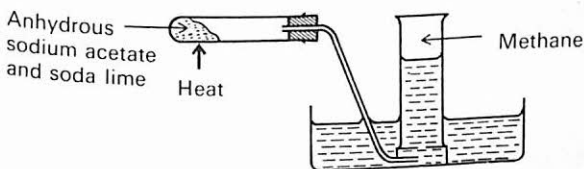
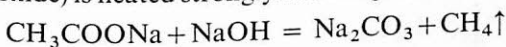
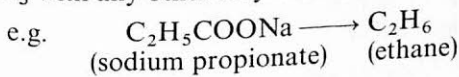


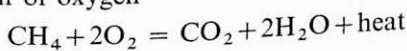
fig. 37 The preparation of methane

This method may be used to prepare any member of the series by replacing CH_3 with any other alkyl radical,

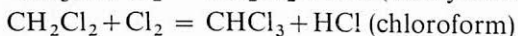
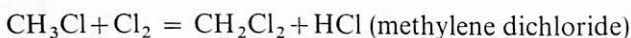
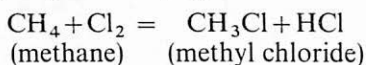


Properties of paraffins (using methane as a typical member)

a They burn in air or oxygen



b They react with chlorine (in the presence of ultra-violet light) to form a variety of products – halogen derivatives of the paraffins. This type of reaction is called *substitution* as chlorine atoms take the place of hydrogen atoms, e.g.



This is a chain reaction, continuing until all four hydrogen atoms are replaced.

Paraffins of higher molecular weight than methane produce many more products of chlorination.

Olefines (Alkenes)

These also are hydrocarbons.

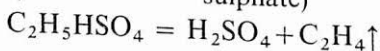
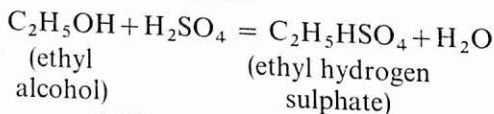
General formula: C_nH_{2n}

	Molecular formula	Structural formula	Molecular weight
Ethylene (ethene)	C_2H_4	$\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} \\ & / & \diagdown \\ \text{H} & & \text{H} \end{array}$	28
Propylene (propene)	C_3H_6	$\begin{array}{c} \text{H} & \text{H} & & \\ & & & \\ \text{H}-\text{C} & -\text{C} & =\text{C} & \\ & & \diagup & \diagdown \\ \text{H} & & \text{H} & \text{H} \end{array}$	42

Note: each compound in this series contains one double bond between two carbon atoms.

Preparation of ethylene (ethene)

A mixture of 1 part ethyl alcohol and 2 parts concentrated sulphuric acid is heated to 170°C and the gas evolved is passed through sodium hydroxide solution to free it from sulphur dioxide. Sweet smelling ethylene gas is collected over water.



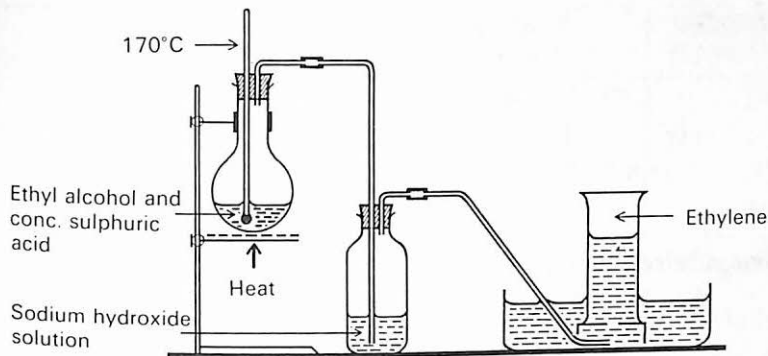
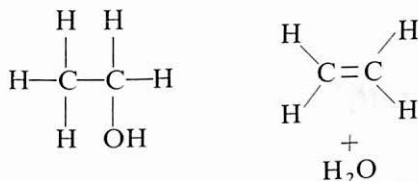


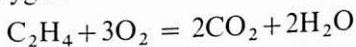
fig. 38 The preparation of ethylene

The overall reaction is the dehydration of ethyl alcohol.



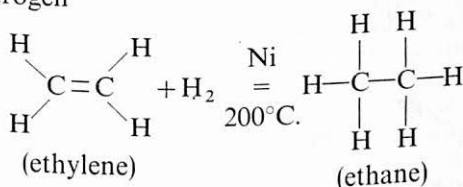
Properties of olefines, e.g. ethylene

a Burns in air or oxygen.

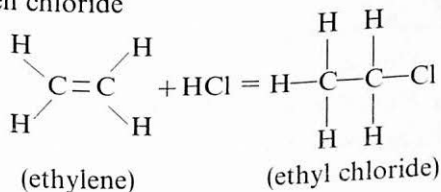


b Addition reactions. Olefines contain a double bond and are therefore said to be unsaturated. Thus other molecules can be added, using up all four valencies of carbon.

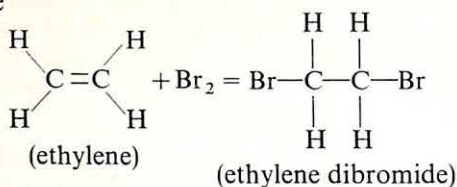
i Hydrogen



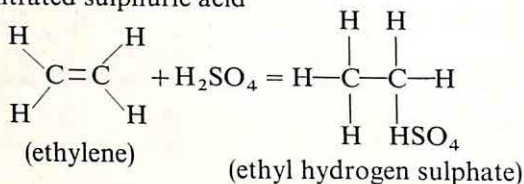
ii Hydrogen chloride



iii Bromine



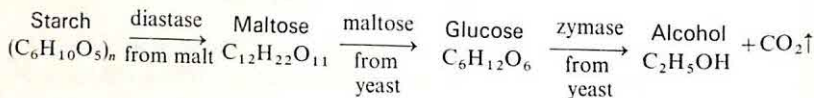
iv Concentrated sulphuric acid



Alcohols

General formula : $\text{C}_n\text{H}_{2n+1}\text{OH}$

Preparation of ethyl alcohol (ethanol), a typical member of the series. Ethyl alcohol is usually made from carbohydrates by fermentation, using organic catalysts called enzymes.

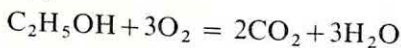


Ethyl alcohol is the substance known as 'alcohol' in everyday life. It is produced by the above method as a very dilute aqueous mixture and, depending on the conditions and additives, the result is one of several well-known alcoholic beverages.

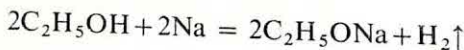
For industrial use the dilute mixture is carefully distilled, giving under various conditions methylated spirit, surgical spirit or absolute alcohol.

Properties of ethyl alcohol (ethanol)

a Burns in air or oxygen.



b Reaction with sodium metal.

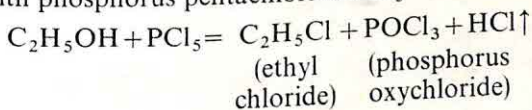


This is analogous to the reaction of sodium with water but is much less vigorous (see page 25).

	Molecular formula	Structural formula	Molecular weight
Methyl alcohol (methanol)	CH_3OH	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	32
Ethyl alcohol (ethanol)	$\text{C}_2\text{H}_5\text{OH}$	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	46
Propyl alcohol (propanol)	$\text{C}_3\text{H}_8\text{OH}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{OH} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$ <p>(<i>n</i>-propanol)</p> $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$ <p>(iso-propanol)</p>	60

Each of these contains the $-\text{OH}$ radical attached to an alkyl radical.

c Reaction with phosphorus pentachloride PCl_5

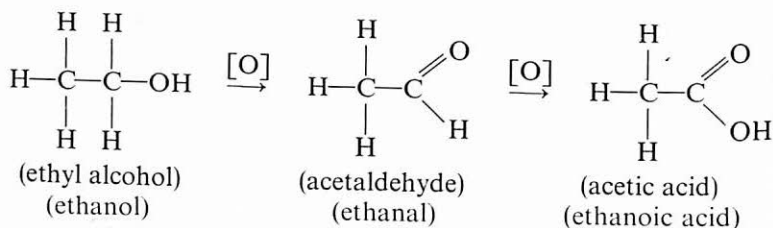


The overall reaction is the replacement of $-\text{OH}$ by $-\text{Cl}$ and the evolution of hydrogen chloride, and serves as a test for an organic $-\text{OH}$ group.

d Reaction with concentrated sulphuric acid: (see preparation of ethylene).

e Oxidation. The oxidising agent is chromic acid, which is made by

adding concentrated sulphuric acid to a concentrated solution of potassium dichromate in water.



Acids

These are commonly known as fatty acids or carboxylic acids.

General formula: $\text{C}_n\text{H}_{2n+1}\text{COOH}$

	Molecular formula	Structural formula	Molecular weight
Formic acid (methanoic acid)	$\text{H}.\text{COOH}$	$\begin{array}{c} \text{O} \\ // \\ \text{H}-\text{C} \\ \backslash \\ \text{OH} \end{array}$	46
Acetic acid (ethanoic acid)	$\text{CH}_3.\text{COOH}$	$\begin{array}{c} \text{H} \quad \quad \text{O} \\ \quad \quad // \\ \text{H}-\text{C}-\text{C} \\ \quad \quad \backslash \\ \text{H} \quad \quad \text{OH} \end{array}$	60
Propionic acid (propanoic acid)	$\text{C}_2\text{H}_5\text{COOH}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \quad \text{O} \\ \quad \quad \quad // \\ \text{H}-\text{C}-\text{C}-\text{C} \\ \quad \quad \quad \backslash \\ \text{H} \quad \text{H} \quad \quad \text{OH} \end{array}$	74

They all contain the $\begin{array}{c} \text{O} \\ // \\ -\text{C} \\ \backslash \\ \text{OH} \end{array}$ group (Carboxyl group) and an alkyl radical.

Preparation of acetic acid, a typical member.

Acids may be prepared by prolonged oxidation of ethyl alcohol with chromic acid. A reflux condenser in which cold water is circulating prevents the loss of alcohol vapour or acetaldehyde vapour as the reaction is proceeding.

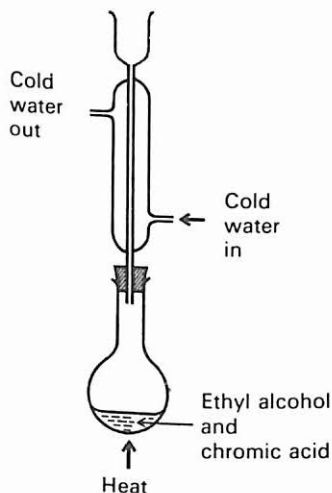
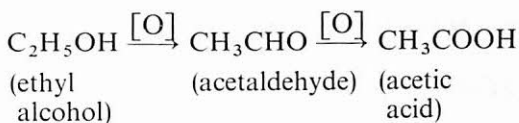
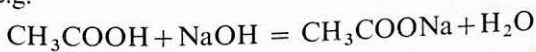


fig. 39 The preparation of acetic acid

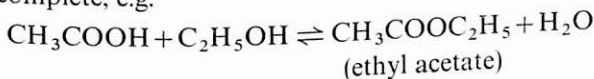
Properties of acetic acid

a Reaction with alkalis. They behave as normal acids and form salts and water, e.g.



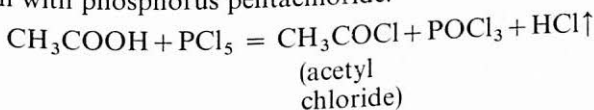
The reaction is ionic. $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

b Reaction with alcohols. This reaction is similar to (a), but is not ionic and is incomplete, e.g.



Ethyl acetate is an ester and the process is called esterification. The addition of a small quantity of concentrated sulphuric acid removes the water and prevents the back reaction from taking place.

c Reaction with phosphorus pentachloride.



Again an $-\text{OH}$ group is replaced by a chlorine atom and hydrogen chloride is formed (see also p. 49).

7 Laws governing the behaviour of gases

BOYLE'S LAW

The pressure of a fixed mass of gas is inversely proportional to its volume when the temperature remains constant.

$$P \propto \frac{1}{V}; T \text{ constant}$$

$$\therefore P = \frac{k}{V} \quad (\text{where } k \text{ is a constant})$$

$\therefore PV$ is constant when T is constant

CHARLES' LAW

The volume of a fixed mass of gas is proportional to its absolute temperature when the pressure remains constant.

$$V \propto T \quad P \text{ constant}$$

$$\therefore V = kT \quad (\text{where } k \text{ is a constant})$$

This means that there is a temperature where the volume of a gas is theoretically zero. This is approximately -273°C . and is called the *absolute zero*, giving rise to the Absolute or Kelvin scale of temperature. Thus $20^\circ\text{C} = (273 + 20)\text{K} = 293\text{K}$.

N.T.P. (S.T.P.) AND CONVERSION OF GAS VOLUMES

The two laws above may be combined to give:

$$PV = RT \quad (\text{where } R \text{ is the constant for the gram molecule})$$

$$\therefore \frac{PV}{T} = R$$

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Since gas volumes fluctuate so widely with changes of temperature and pressure, it is often necessary to convert a volume of gas to what it would be under standard temperature and pressure conditions (s.t.p.). These are 0°C (273K) and 760 mm of mercury (sometimes known as N.T.P.—normal temperature and pressure).

Example: To convert 300 cm^3 of gas measured at 21°C and 740 mm of mercury to s.t.p.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \frac{740 \times 300}{(273 + 21)} = \frac{760 \times V_2}{273}$$

$$\therefore V_2 = \frac{740 \times 300 \times 273}{760 \times 294} \text{ cm}^3$$

$$= 271.3 \text{ cm}^3$$

GAY - LUSSAC'S LAW OF COMBINING VOLUMES

When gases react under constant temperature and pressure conditions, they do so in a simple ratio by volume and the products, if gaseous, are also in a simple ratio to each other and to the reactants, e.g.

Hydrogen + chlorine = hydrogen chloride
1 volume 1 volume 2 volumes

Hydrogen + oxygen = water (steam)
2 volumes 1 volume 2 volumes

Sulphur dioxide + oxygen = sulphur trioxide
2 volumes 1 volume 2 volumes

Carbon + oxygen = carbon dioxide
(solid) 1 volume 1 volume

Carbon monoxide + steam = carbon dioxide + hydrogen
1 volume 1 volume 1 volume 1 volume

Nitrogen + hydrogen = ammonia
1 volume 3 volumes 2 volumes

AVOGADRO'S HYPOTHESIS

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

Thus if 2 volumes of hydrogen + 1 volume of oxygen = 2 volumes of steam

then 2 molecules of hydrogen + 1 molecule of oxygen = 2 molecules of steam

The atomicity of gases (number of atoms per molecule)

Hydrogen + chlorine = hydrogen chloride
1 volume + 1 volume \rightarrow 2 volumes

By Avogadro's Hypothesis

1 molecule + 1 molecule \rightarrow 2 molecules

Each molecule of hydrogen chloride must contain some hydrogen and some chlorine, and *since part of an atom cannot take part in a reaction*, the hydrogen molecule and the chlorine molecule must both contain at least 2 atoms, i.e. one atom of each going to each hydrogen chloride molecule.

There is no evidence to prove that there are *more* than two atoms in

each of these molecules; there is independent evidence, outside the scope of this text, to prove that there are *only* two.

THE VAPOUR DENSITY OF GASES

The vapour density (V.D.) of a gas or vapour is the weight of a volume of the gas divided by the weight of the same volume of hydrogen under the same conditions of temperature and pressure.

$$\begin{aligned} \text{V.D.} &= \frac{\text{weight of 1 volume of gas}}{\text{weight of 1 volume of hydrogen}} \\ &= \frac{\text{weight of } n \text{ molecules of gas}}{\text{weight of } n \text{ molecules of hydrogen}} && \text{(by Avogadro's Hypothesis)} \\ &= \frac{\text{weight of 1 molecule of gas}}{\text{weight of 1 molecule of hydrogen}} \\ &= \frac{\text{Molecular weight of the gas}}{2} \end{aligned}$$

It has been established that the hydrogen molecule is diatomic, and each hydrogen atom has a weight of 1.

Thus the *molecular weight of a gas or vapour is twice its vapour density*. Since the density of a gas is relatively easy to measure, this provides a simple method of determining molecular weight.

THE GRAM MOLECULAR VOLUME (G.M.V.) OR MOLAR VOLUME

The density of hydrogen is easily measured, and so the volume occupied by 1 gram molecule or 1 mole at s.t.p. is easily calculated and is found to be 22.4 litres. From Avogadro's Hypothesis it follows that:

The gram molecular weight of any gas occupies a volume of 22.4 litres at s.t.p.

22.4 litres is called the gram molecular volume (G.M.V.) or molar volume and is of importance in converting weights of gases to volumes and vice-versa (see page 58). Thus, at s.t.p.

2 g of H_2 occupies 22.4 l
28 g of N_2 occupies 22.4 l
44 g of CO_2 occupies 22.4 l.

DETERMINING OF THE FORMULAE OF VARIOUS GASES

a Hydrogen chloride

Equal volumes of hydrogen and chlorine are introduced into the apparatus shown in fig. 40.

Taps A and C are closed and tap B is opened, with the apparatus in diffuse sunlight, to allow the gases to react. After some time, A is opened

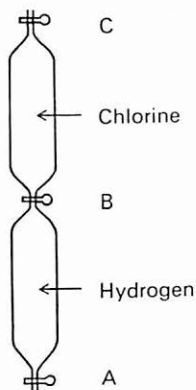


fig. 40

under mercury. Nothing happens showing that no pressure (and therefore volume) change has occurred. Tap A is then opened under water which completely fills the apparatus, showing that a very soluble gas (hydrogen chloride) has been formed.

$\therefore 1 \text{ volume hydrogen} + 1 \text{ volume chlorine} = 2 \text{ volumes hydrogen chloride}$

By Avogadro

$1 \text{ molecule hydrogen} + 1 \text{ molecule chlorine} = 2 \text{ molecules hydrogen chloride}$

$\therefore 2 \text{ atoms hydrogen} + 2 \text{ atoms chlorine} = 2 \text{ molecules hydrogen chloride}$

$\therefore 1 \text{ atom hydrogen} + 1 \text{ atom chlorine} = 1 \text{ molecule hydrogen chloride}$

\therefore The formula of hydrogen chloride is HCl.

b Steam

An electric spark is passed through a mixture of 2 volumes of hydrogen and 1 volume of oxygen, contained over mercury in a graduated tube (eudiometer) at a temperature higher than 100°C . It is found that the volume decreases by $\frac{1}{3}$ if the temperature is kept constant.

$\therefore 2 \text{ volumes hydrogen} + 1 \text{ volume oxygen} = 2 \text{ volumes steam}$

By Avogadro

$2 \text{ molecules hydrogen} + 1 \text{ molecule oxygen} = 2 \text{ molecules steam}$

$\therefore 4 \text{ atoms hydrogen} + 2 \text{ atoms oxygen} = 2 \text{ molecules steam}$

$\therefore 2 \text{ atoms hydrogen} + 1 \text{ atom oxygen} = 1 \text{ molecule steam}$

\therefore The formula of steam (water) is H_2O .

c Carbon dioxide and sulphur dioxide

A small sample of carbon or sulphur is burned in excess oxygen over mercury in a graduated tube. After cooling to the original conditions there is no change in volume.

∴ 1 volume carbon dioxide is formed from 1 volume oxygen

By Avogadro

1 molecule carbon dioxide is formed from 1 molecule oxygen

∴ 1 molecule carbon dioxide is formed from 2 atoms oxygen

∴ The formula of carbon dioxide is C_xO_2 .

But the V.D. of carbon dioxide is 22.

∴ Molecular weight is 44.

(C = 12; O = 16).

$$\therefore 12x + 32 = 44$$

$$x = 1$$

∴ The formula of carbon dioxide is CO_2 .

Similarly, the formula of sulphur dioxide is SO_2 .

8 Atomic weights and equivalents (combining weights)

As the study of chemistry developed it was found necessary to obtain some idea of the weights of atoms. Since these are infinitesimal, it is only necessary to compare their weights, and the standard chosen for this was hydrogen, the element with the lightest atom.

Atomic weight

The atomic weight of an element is the weight of one atom of the element on a scale on which the hydrogen atom weighs one (unit).

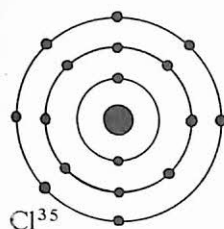
This standard was later changed to oxygen, so changing slightly all atomic weights. It was subsequently changed to a stable isotope of carbon which is the international standard today.

THE RELATIONSHIP BETWEEN MASS NUMBER AND ATOMIC WEIGHT

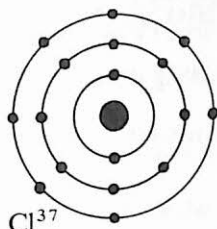
Mass number (see page 6) is the total number of protons and neutrons in the nucleus of an atom.

It would appear that mass number and atomic weight should be the same, since the hydrogen atom contains one proton and no neutrons, i.e. it has a mass number of 1. The fact that in most cases they are not

the same is due to the existence of *isotopes*, i.e. atoms with the same electronic structure but different numbers of neutrons in the nucleus, e.g. chlorine consists of two isotopes.



17 electrons
17 protons
18 neutrons



17 electrons
17 protons
20 neutrons

These are chemically the same, due to their identical electronic structures. Since they are of different weights their existence means that the measured atomic weight is a weighted average of the weight of all atoms of the element.

For example, chlorine has an atomic weight of 35.5 showing that there is more Cl^{35} than Cl^{37} in existence.

THE RELATIONSHIP BETWEEN EQUIVALENT (COMBINING WEIGHT) AND ATOMIC WEIGHT

Water contains
Combining weights
(experimental)

hydrogen combined with oxygen.

Atomic weights

Factor involved

1
1
1

8
16
2

Magnesium oxide contains

magnesium combined with oxygen.

Combining weights
(experimental)

Atomic weights

Factor involved

12
24
2

8
16
2

The factor in each case is the combining number or valency of the element.

Thus
$$\frac{\text{atomic weight}}{\text{equivalent}} = \text{valency}$$

or
$$\frac{\text{atomic weight}}{\text{combining weight}} = \text{combining number}$$

The equivalents can be determined accurately by various means and accurate values of atomic weights can be calculated from them.

DULONG AND PETIT'S LAW

For metals at normal temperature,

Atomic weight \times specific heat ≈ 6.4

Consider an element of specific heat 0.09 and equivalent 32.

Then atomic weight $\times 0.09 \approx 6.4$

$$\therefore \text{Approximate atomic weight} = \frac{6.4}{0.09} = 71.1$$

$$\frac{\text{Approximate atomic weight}}{\text{Equivalent}} = \frac{71.1}{32} = 2.2 = \text{approximate valency}$$

The valency must be a whole number and the most likely value here is 2.

$$\begin{aligned}\therefore \text{Accurate atomic weight} &= \text{equivalent} \times \text{valency} \\ &= 32 \times 2 \\ &= 64\end{aligned}$$

The use of atomic weights in calculations

For practical purposes the atomic weight is expressed in grams; it thus becomes the *gram atomic weight*.

a Calculation of molecular weight or formula weight, e.g.

Magnesium oxide MgO
Atomic weights 24 + 16

Gram formula weight = 40 g

Washing soda $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

Atomic weights $(2 \times 23) + 12 + (3 \times 16) + 10[2 + 16]$

Gram formula weight = 286 g

Example: Calculate the weight of lead formed when 22.3 g of lead (II) oxide is reduced by hydrogen (Pb = 207; O = 16).

Write a balanced equation. $\text{PbO} + \text{H}_2 = \text{Pb} + \text{H}_2\text{O}$

Extract the relevant parts. $\text{PbO} \rightarrow \text{Pb}$

Calculate the formula weights. $(207 + 16) \rightarrow 207$

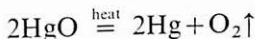
\therefore 223 g lead (II) oxide produces 207 g lead on reduction

\therefore 22.3 g lead (II) oxide produces 20.7 g lead on reduction

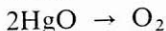
This type of calculation may involve a gas volume.

Example: Calculate the volume of oxygen, measured at 27°C and 750 mm pressure, formed when 4.32 g of mercury (II) oxide is completely decomposed by heat (Hg = 200; O = 16; the gram molecular volume is 22.4 l at s.t.p.).

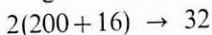
Write a balanced equation.



Extract the relevant parts.



Calculate the formula weights.



\therefore 432 g mercury (II) oxide produce 32 g oxygen = 22.4 l at s.t.p.

\therefore 4.32 g mercury (II) oxide produce 224 cm³ oxygen at s.t.p.

Convert 224 cm³ from s.t.p. to the stated conditions.

$$\begin{aligned}\frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\ \frac{760 \times 224}{273} &= \frac{750 \times V_2}{300} \\ \therefore V_2 &= \frac{760 \times 224 \times 300}{750 \times 273} \\ &= 249.4 \text{ cm}^3\end{aligned}$$

Thus 4.32 g mercury (II) oxide when heated produces 249.4 cm³ oxygen at 27°C and 750 mm.

b Calculation of percentage composition

Example: Calculate the percentage composition of magnesium oxide (Mg = 24; O = 16).

$$\begin{aligned}\text{MgO} \\ 24 + 16 &= 40 \\ \% \text{Mg} &= \frac{24}{40} \times 100\% \\ &= 60\% \\ \% \text{O} &= \frac{16}{40} \times 100\% \\ &= 40\%\end{aligned}$$

Example: Calculate the percentage composition of ammonium sulphate. (N = 14; H = 1; S = 32; O = 16)

$$\begin{aligned}(\text{NH}_4)_2\text{SO}_4 \\ 2[14 + 4] + 32 + (4 \times 16) &= 132 \\ \% \text{N} &= \frac{28}{132} \times 100\%; & \% \text{H} &= \frac{8}{132} \times 100\%; \\ &= 21.22\% & &= 6.06\% \\ \% \text{S} &= \frac{32}{132} \times 100\%; & \% \text{O} &= \frac{64}{132} \times 100\% \\ &= 24.24\% & &= 48.48\%\end{aligned}$$

c Determination of empirical and molecular formulae

Example: The percentage composition of a compound X is carbon 40%, hydrogen 6.67% and oxygen 53.33%. If the vapour density of the compound is 30, determine its empirical formula and hence its molecular formula. (C = 12; H = 1; O = 16)

	% = relative weights	Relative numbers of atoms	Simplest ratio
C	40	$\frac{40}{12} = 3.33$	1
H	6.67	$\frac{6.67}{1} = 6.67$	2
O	53.33	$\frac{53.33}{16} = 3.33$	1

∴ The simplest (empirical) formula is CH_2O .

Vapour density of X (V.D.) = 30

∴ Molecular weight of X = $30 \times 2 = 60$ (see page 54).

Molecular weight of $\text{CH}_2\text{O} = 12 + 2 + 16 = 30$

∴ Molecular formula of X is $(\text{CH}_2\text{O})_2$ or $\text{C}_2\text{H}_4\text{O}_2$.

Volumetric analysis

This is a process in which solutions of known concentration are used to find the concentrations of solutions which react with them, e.g. an acid of known concentration can be used to find the concentration of an alkaline solution.

The gram equivalent of an acid is the number of grams of the acid which contain one gram of replaceable hydrogen.

Examples:

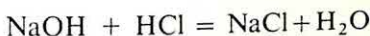
Acid	Hydrochloric	Nitric	Sulphuric	Acetic
Formula	HCl	HNO_3	H_2SO_4	CH_3COOH
Atomic weights	1 + 35.5	1 + 14 + 48	2 + 32 + 64	12 + 3 + 12 + 32 + 1
Gram formula weights	36.5	63	98	60
Gram equivalent (g.E.)	$\frac{36.5}{1} = 36.5 \text{ g}$	$\frac{63}{1} = 63 \text{ g}$	$\frac{98}{2} = 49 \text{ g}$	$\frac{60}{1} = 60 \text{ g}$

Note: the number of replaceable hydrogen atoms is known as the basicity of the acid and the gram equivalent = $\frac{\text{gram formula}}{\text{basicity}}$.

The gram equivalent of a base is the number of grams of the base which react with one gram equivalent of any acid. (This can be applied to metals and carbonates as well as to oxides and hydroxides.)

Examples:

a Sodium hydroxide.

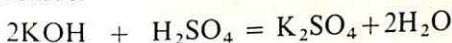


$$23 + 16 + 1 \equiv 36.5$$

$\therefore 40 \text{ g NaOH} \equiv 36.5 \text{ g HCl}$, which is the g.E. of hydrochloric acid.

\therefore The g.E. of sodium hydroxide is 40 g.

b Potassium hydroxide.



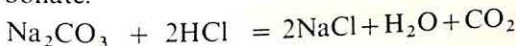
$$2(39 + 16 + 1) \equiv 98$$

$$112 \text{ g} \equiv 98 \text{ g}$$

$\therefore 56 \text{ g KOH} \equiv 49 \text{ g H}_2\text{SO}_4$ which is the g.E. of sulphuric acid.

\therefore The g.E. of potassium hydroxide is 56 g.

c Sodium carbonate.



$$46 + 12 + 48 \equiv 2 \times 36.5$$

$$106 \text{ g} \equiv 2 \times 36.5 \text{ g}$$

$$53 \text{ g} \equiv 36.5 \text{ g}$$

\therefore The g.E. of sodium carbonate is 53 g.

Similarly

The g.E. of sodium hydrogen carbonate (NaHCO_3) = 84 g.

The g.E. of potassium hydrogen carbonate (KHCO_3) = 100 g.

NORMALITY

A normal solution (N) is one which contains 1 gram equivalent of pure substance per litre of solution. (1 litre = 1 dm^3 or 1000 cm^3 .)

Example:

The gram equivalent of sodium hydroxide is 40.

\therefore A solution containing 40 g per litre is a normal (N) solution.

\therefore A solution containing 4 g per litre is a decinormal $\left(\frac{\text{N}}{10}\right)$ solution.

The latter can also be expressed as 0.1 N and it is obvious that the normality of a solution can have any value, e.g. 0.126 N.

It is also obvious from the above that

Normality \times gram equivalent = concentration in g per litre

$$0.1 \text{ N} \times 40 = 4 \text{ g per litre}$$

$$0.126 \text{ N} \times 40 = 5.04 \text{ g per litre}$$

MOLARITY

A molar solution (M) is one which contains 1 gram molecule (1 mole) of pure substance per litre of solution.

This is merely an alternative method of expressing the concentration of a solution and avoids the necessity of using equivalents. The molarity of a solution is the same as its normality in only some cases (e.g. HCl, NaOH) but not in others (e.g. Na_2CO_3 , H_2SO_4), so care must be taken to refrain from indiscriminate use of the two terms.

A standard solution is a solution of known concentration, and the process which makes use of its value to find the concentration of another solution is known as a titration.

The g.E. of hydrochloric acid \equiv the g.E. of sodium hydroxide

$\therefore 36.5 \text{ g of hydrochloric acid} \equiv 40 \text{ g of sodium hydroxide}$

\therefore From the definition of normality

$$1000 \text{ cm}^3 \text{ N HCl} \equiv 1000 \text{ cm}^3 \text{ N NaOH}$$

$$\therefore 25 \text{ cm}^3 \frac{\text{N}}{10} \text{ HCl} \equiv 25 \text{ cm}^3 \frac{\text{N}}{10} \text{ NaOH}$$

$$\begin{array}{ccc} \text{Volume of} & \times & \text{normality of} \\ \text{acid} & & \text{acid} \end{array} = \begin{array}{ccc} \text{volume of} & \times & \text{normality of} \\ \text{base} & & \text{base} \end{array}$$
$$V_a N_a = V_b N_b$$

If one of these is unknown, say N_b , it can be found by doing a titration and a simple calculation.

A TYPICAL TITRATION

Find the normality and concentration in grams per litre of the given hydrochloric acid solution, using the 0.105 N sodium carbonate provided.

Apparatus required: burette, 25 cm³ pipette, 3 conical flasks, wash-bottle, white tile and indicator bottle.

Method

- a Wash out all apparatus with distilled water.
- b Wash the burette with a little of the acid solution and fill with acid.
- c Draw a little sodium carbonate solution into the pipette, run it around the inside of the pipette and allow it to drain.
- d Pipette 25 cm³ of the sodium carbonate solution into a conical flask

and add 3 drops of methyl orange (screened methyl orange if preferred).
 e Record the initial burette reading and add acid from the burette slowly and carefully with washing until the colour of the indicator just changes. Record the final burette reading and subtract to find the volume of acid required.

f Repeat this process three times and average two readings which are within 0.10 cm^3 of each other.

Calculation

Assume that the average titre (result of titration) is 22.50 cm^3 .

$\therefore 22.50 \text{ cm}^3$ hydrochloric acid = 25.00 cm^3 0.105 N sodium carbonate.

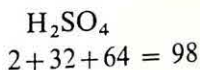
The acid must be of higher concentration than the carbonate (since

less of it was required) by a factor of $\frac{25.00}{22.50}$.

$$\begin{aligned}\therefore \text{Normality of acid} &= \frac{25.00}{22.50} \times 0.105 \text{ N} \\ &= 0.117 \text{ N}\end{aligned}$$

$$\begin{aligned}\text{Concentration in g per litre} &= 0.117 \times 36.5 \\ &= 4.27 \text{ g per litre}\end{aligned}$$

Further example: 21.55 cm^3 of a solution of sulphuric acid containing 5 g per litre was required by 25 cm^3 of potassium hydroxide solution for complete neutralisation. Find the normality and concentration in grams per litre of the potassium hydroxide. ($\text{H} = 1$; $\text{S} = 32$; $\text{O} = 16$; $\text{K} = 39$)

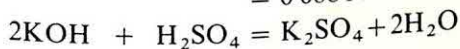


$$\text{The g.E. of H}_2\text{SO}_4 \text{ is } \frac{98}{2} = 49$$

$$\therefore \text{Normality of sulphuric acid} = \frac{5}{49} \text{ N}$$

$\therefore 21.55 \text{ cm}^3$ $\frac{5}{49} \text{ N}$ sulphuric acid = 25 cm^3 potassium hydroxide solution

$$\begin{aligned}\therefore \text{Normality of KOH} &= \frac{21.55}{25} \times \frac{5}{49} \\ &= 0.088 \text{ N}\end{aligned}$$



$$2(39 + 16 + 1) \equiv 98$$

$$\therefore 56 \equiv 49$$

\therefore The g.E. of KOH is 56 g .

$$\begin{aligned}\text{Strength in g per litre} &= 0.088 \times 56 \\ &= 4.93 \text{ g per litre}\end{aligned}$$

Faraday's laws of electrolysis

THE FIRST LAW OF ELECTROLYSIS

The mass of a substance liberated in electrolysis (see page 13) is proportional to the quantity of electricity passed.

$$m \text{ (grams)} \propto Q \text{ (coulombs)}$$

$$m \propto It \quad [Q \text{ coulombs} = I \text{ amperes} \times t \text{ seconds}]$$

$$m = ZIt$$

Z is a constant for a particular element and is called the *electrochemical equivalent* of the element.

Examples:

a Calculate the mass of copper deposited on the cathode when a current of 2 A is passed through copper sulphate solution for half an hour. (The electrochemical equivalent of copper is 0.000 33 g per coulomb.)

$$\begin{aligned} m &= ZIt \\ &= 0.000\ 33 \times 2 \times 1800 \\ &= 1.188 \text{ g} \end{aligned}$$

b Calculate the time required to produce 100 cm³ of hydrogen, at 25°C and 750 mm pressure, by passing 2 A through dilute sulphuric acid in a Hoffmann voltameter. (E.C.E. for hydrogen is 0.000 010 5 g per coulomb; the gram molecular volume is 22.4 l at N.T.P.)

Convert the volume to N.T.P.

$$\begin{aligned} \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\ \frac{100 \times 750}{298} &= \frac{760 \times V_2}{273} \end{aligned}$$

$$V_2 = \frac{100 \times 750 \times 273}{298 \times 760} = 90.42 \text{ cm}^3 \text{ at N.T.P.}$$

From G.M.V. at N.T.P. :- 22.4 litres weigh 2 grams.

$$90.42 \text{ cm}^3 \text{ weigh } \frac{2 \times 90.42}{22\ 400} \text{ g}$$

$$m = ZIt$$

$$t = \frac{m}{ZI}$$

$$= \frac{2 \times 90.42}{22\ 400 \times 2 \times 0.000\ 010\ 5}$$

$$= 384.5 \text{ seconds} = 6 \text{ minutes } 24.5 \text{ seconds.}$$

Note: It was necessary to convert the volume to N.T.P. since the conversion factor (G.M.V.) was under N.T.P. conditions. Pressure and volume changes have no effect on the *mass* of a gas, only on its volume.

THE SECOND LAW OF ELECTROLYSIS

When the same quantity of electricity is passed through different solutions of electrolytes, the masses of substances liberated are proportional to their chemical equivalents.

This can be proved by setting up three voltmeters in series, passing a current through them for a certain time and measuring the weights of the substances liberated.

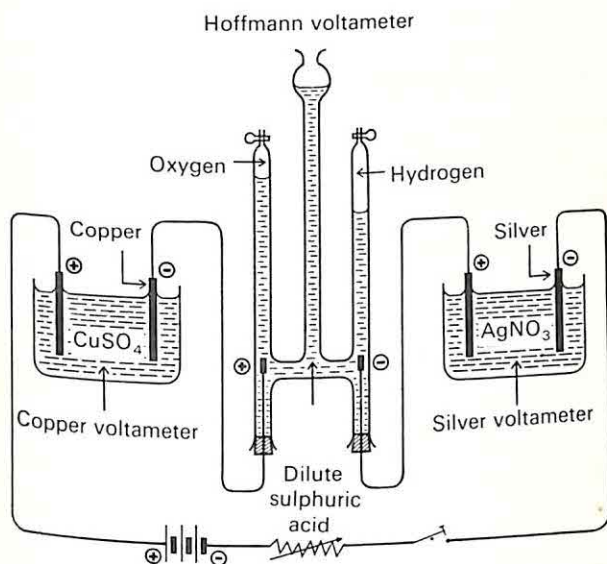


fig. 41 Experiment to prove Faraday's Second Law of Electrolysis

The weights of copper, hydrogen, oxygen and silver are in the ratio of 31.75 : 1 : 8 : 108 which are the equivalents of the elements. The gram atomic weights are 63.5 : 1 : 16 : 108, and since the mass liberated is proportional to the quantity of electricity (First Law), copper and oxygen both seem to need twice as many coulombs of electricity as hydrogen and silver for the liberation of one gram atom. This is because copper and oxygen have valencies of two and hydrogen and silver have valencies of one.

Example: Calculate the weight of silver deposited on the cathode of a

silver voltameter in the same time as 119.3 cm^3 of hydrogen at 27°C and 784 mm pressure are evolved in a Hoffmann voltameter in series with it. ($\text{Ag} = 108$; $\text{H} = 1$; G.M.V. = 22.4 l at s.t.p.)
Convert 119.3 cm^3 to s.t.p.

$$\begin{aligned}\frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\ \frac{119.3 \times 784}{300} &= \frac{V_2 \times 760}{273} \\ V_2 &= \frac{119.3 \times 784 \times 273}{300 \times 760} \\ &= 112 \text{ cm}^3 \text{ at N.T.P.}\end{aligned}$$

$22\,400 \text{ cm}^3$ of hydrogen at N.T.P. weighs 2 grams .

112 cm^3 of hydrogen at N.T.P. weighs $\frac{2 \times 112}{22\,400} \text{ grams}$.
 $= 0.01 \text{ grams}$.

By the Second Law the masses liberated are in proportion to the chemical equivalents.

Atomic weights	$\text{Ag} = 108$	$\text{H} = 1$
Equivalents	108	1
Weights liberated	$x \text{ grams}$	0.01 grams

$$\therefore \frac{108}{x} = \frac{1}{0.01}$$

$$x = 1.08 \text{ grams}$$

The weight of silver deposited is 1.08 grams .

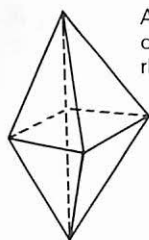
9 Sulphur

OCCURRENCE

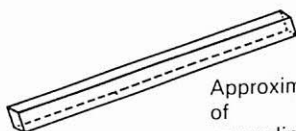
a As the element in the Southern states of the U.S.A., where the sulphur deposits are at a considerable depth in the earth, and are brought to the surface by a process which involves melting the sulphur underground by superheated water and forcing it (as a liquid) to the surface through concentric pipes, where it solidifies in a pure state. The process is known as the Frasch Process.

b As the element in volcanic deposits which occur on or near the surface in Sicily. The sulphur is purified by a process similar to distillation.

c As various metal sulphides, e.g. zinc blende, ZnS , cinnabar, HgS .



Approximate shape
of
rhombic sulphur crystal



Approximate shape
of
monoclinic sulphur crystal

fig. 42 Allotropes of sulphur

ALLOTROPE OF SULPHUR

Sulphur can exhibit allotropy (compare carbon p. 31) and can be produced in the following different physical states.

Rhombic sulphur(α) Formed as squat yellow crystals by the evaporation of a solution of sulphur in carbon disulphide.

Monoclinic sulphur(β) (Prismatic) Formed as long yellow needle shaped crystals when sulphur is heated until it just melts and then allowed to cool slowly.

Plastic sulphur(γ) Formed as a brown rubbery mass when sulphur is heated until it boils and is then poured into cold water.

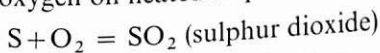
Amorphous sulphur(δ) Formed slowly as a fine yellow suspension when dilute acid is added to sodium thiosulphate solution.

PROPERTIES OF SULPHUR

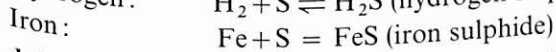
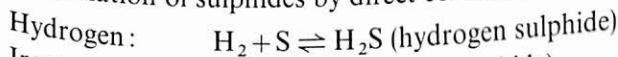
a Action of heat in the absence of air.

Yellow powder $\xrightarrow[115^\circ\text{C.}]{\text{(melts)}}$ amber liquid $\xrightarrow[160^\circ\text{C.}]{\text{(boils)}}$ dark viscous liquid
 $\xrightarrow[444^\circ\text{C.}]{\text{(boils)}}$ dark mobile liquid

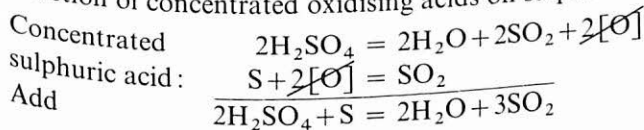
b Action of air or oxygen on heated sulphur.



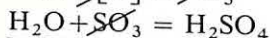
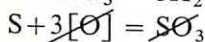
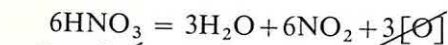
c Formation of sulphides by direct combination.



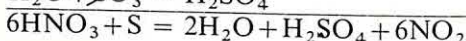
d Action of concentrated oxidising acids on sulphur.



Concentrated
nitric acid:



Add



In each case the sulphur has been oxidised to sulphur dioxide which may then react further.

USES OF SULPHUR

- Preparation of sulphuric acid (see page 73) leading to a variety of products.
- Manufacture of sulphates, sulphites and bisulphites.
- As a fungicide for certain plants.
- Vulcanisation of rubber.

Hydrogen sulphide

PREPARATION OF HYDROGEN SULPHIDE

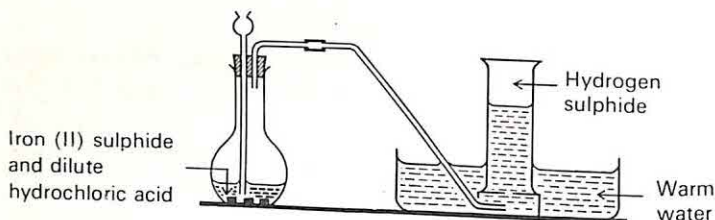


fig. 43 The preparation of hydrogen sulphide

- If only a few gas jars of hydrogen sulphide are required, it may be prepared using the apparatus shown in fig. 43. It is collected over warm water as it is quite soluble in cold water.

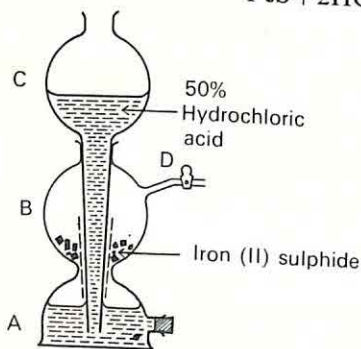
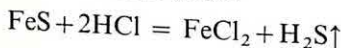


fig. 44 Kipp's apparatus

b If a regular supply of hydrogen sulphide is required for analysis, it is prepared using a Kipp's Apparatus (fig. 44). 50% hydrochloric or 20% sulphuric acid is poured into C, fills A and comes into contact with the ferrous sulphide in B. The reaction starts and hydrogen sulphide is formed in B, displacing the air. When B is full of hydrogen sulphide the tap D is closed and a pressure is set up, forcing the acid down into A, so stopping the reaction. On opening the tap D, hydrogen sulphide can be obtained when required.

Note: This generator can be used to prepare in quantity any gas which is made from a solid and a liquid in the cold.

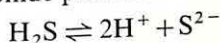
PROPERTIES OF HYDROGEN SULPHIDE

General

- a Colourless gas.
- b Smells of rotten eggs (sulphur present in eggs).
- c Slightly denser than air.
- d Soluble in water.

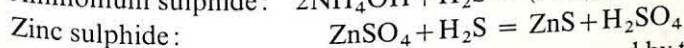
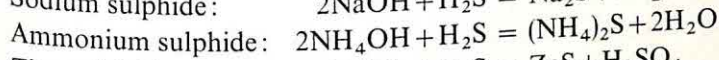
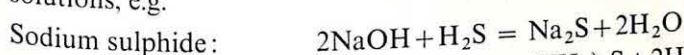
As an acid

In solution hydrogen sulphide produces H^+ ions.



Therefore hydrogen sulphide acts as a dibasic acid and gives rise to a series of salts known as sulphides.

These are formed by the action of hydrogen sulphide on alkalis or salt solutions, e.g.



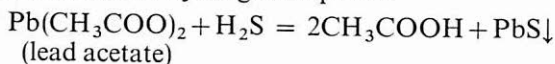
(The zinc sulphide will precipitate if the acid is removed by the addition of alkali.)



Sulphide	Formula	Colour	Solubility	
			In water	In acid
Sodium	Na_2S	colourless	soluble	soluble
Ammonium	$(NH_4)_2S$	yellow	soluble	soluble
Zinc	ZnS	white	insoluble	soluble
Copper	CuS	black	insoluble	insoluble
Lead	PbS	black	insoluble	insoluble

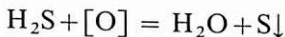
Note: The formation of black lead (II) sulphide on moist lead acetate

paper serves as a test for hydrogen sulphide.

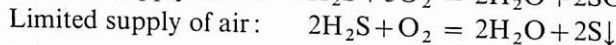
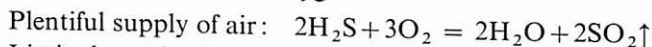


As a reducing agent

Hydrogen sulphide is easily oxidised to sulphur and water and is therefore an effective reducing agent.



i Burns easily in air or oxygen.



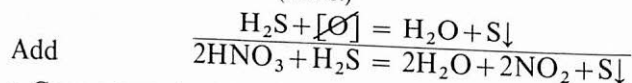
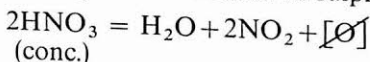
ii Acidified potassium permanganate:

Purple solution $\xrightarrow{\text{H}_2\text{S}}$ colourless solution with pale yellow precipitate

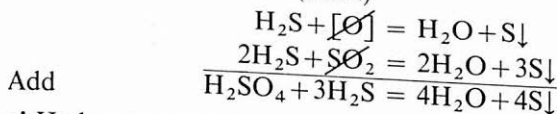
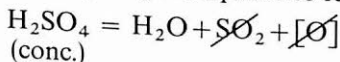
iii Acidified potassium dichromate:

Orange solution $\xrightarrow{\text{H}_2\text{S}}$ green solution with pale yellow precipitate

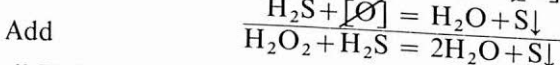
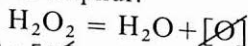
iv Concentrated nitric acid: the nitric acid is reduced to nitrogen dioxide and the hydrogen sulphide is oxidised to sulphur.



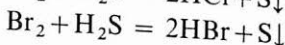
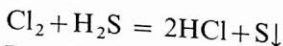
v Concentrated sulphuric acid: the sulphuric acid is reduced to sulphur dioxide, which reacts with the hydrogen sulphide to form sulphur.



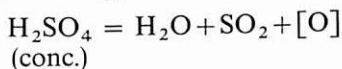
vi Hydrogen peroxide: hydrogen peroxide is reduced to water and hydrogen sulphide oxidised to sulphur.



vii Halogens: chlorine and bromine are both reduced to the corresponding hydrides.



Note: Equations of the type

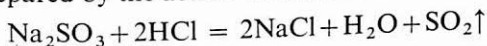


indicate that the reagent is an oxidising agent. *Oxygen gas is not given off during the reaction*, but is available to oxidise any easily oxidised substance which makes contact with the reagent.

Sulphur dioxide

PREPARATION OF SULPHUR DIOXIDE

This gas is prepared by the action of dilute acid on sodium sulphite.



The gas may be dried if necessary by bubbling it through concentrated sulphuric acid.

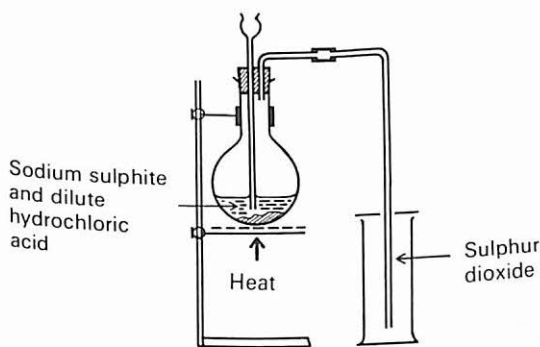


fig. 45 The preparation of sulphur dioxide

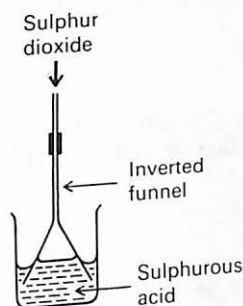


fig. 46

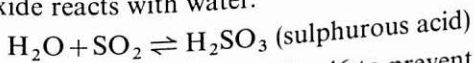
PROPERTIES OF SULPHUR DIOXIDE

General

- a Colourless gas.
- b Pungent.
- c More dense than air (see method of collection, fig. 45).
- d Very soluble in water.

As an acid anhydride (a substance which reacts with water to give an acid).

- a Sulphur dioxide reacts with water.



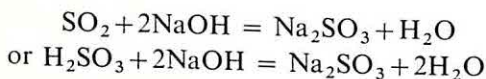
Solution must be effected as shown in fig. 46 to prevent water sucking back into the generating apparatus.

b Sulphur dioxide and sulphurous acid react with alkalis to give sulphites and bisulphites.

Sodium bisulphite:

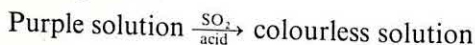


Sodium sulphite:

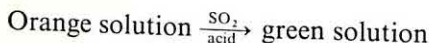


As a reducing agent

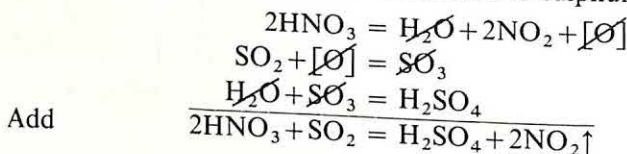
a Potassium permanganate:



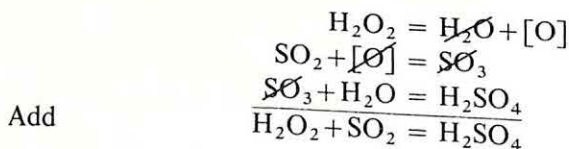
b Potassium dichromate:



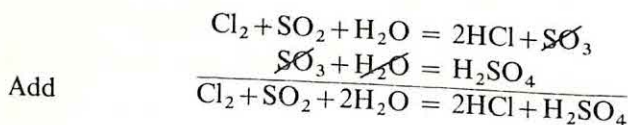
c Concentrated nitric acid: the nitric acid is reduced to nitrogen dioxide and the sulphur dioxide is oxidised to sulphuric acid.



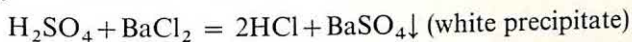
d Hydrogen peroxide: hydrogen peroxide is reduced to water and sulphuric acid is formed.



e Halogens: chlorine, in the presence of moisture, is reduced to hydrogen chloride.



In these reducing actions which are similar to those of hydrogen sulphide, sulphuric acid is produced in each case instead of sulphur, and may be tested for with barium chloride solution.



USES OF SULPHUR DIOXIDE

- The manufacture of sulphuric acid.
- The manufacture of sulphites and bisulphites as general chemicals and for use as bleaching agents for wood pulp in the paper industry.
- As a preservative, e.g. in sausages.

Sulphur trioxide and sulphuric acid

PREPARATION OF SULPHUR TRIOXIDE (THE CONTACT PROCESS)

This is made both industrially and in the laboratory by passing a dry mixture of sulphur dioxide and oxygen over a heated catalyst which was formerly platinum (Pt) but is now mainly vanadium pentoxide (V_2O_5).

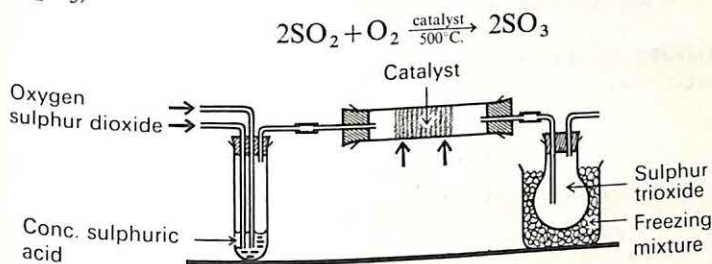
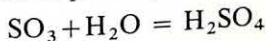


fig. 47 The preparation of sulphur trioxide

(The gases are in *contact* with the catalyst when they react.) Sulphur trioxide reacts with water to produce sulphuric acid.



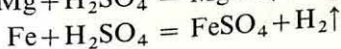
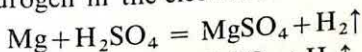
On the industrial scale the vigour of this reaction forms a mist of sulphuric acid drops in the air and constitutes a danger to personnel. It is found more convenient to dissolve the sulphur trioxide in conc. sulphuric acid, producing fuming sulphuric acid (*oleum*) which may be used as such or diluted to the required concentration.

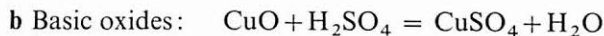
Concentrated sulphuric acid is always diluted by adding the **acid to water**.

PROPERTIES OF SULPHURIC ACID

As an acid (dilute sulphuric acid)

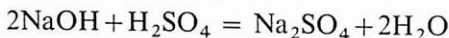
- Metals above hydrogen in the electrochemical series:





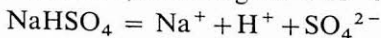
c Hydroxides:

i With an alkali such as sodium hydroxide, normal and acidic salts are formed. This is because sulphuric acid is dibasic and one or both of the hydrogen atoms may be replaced.

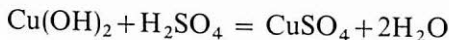


(sodium bisulphate, i.e.
sodium hydrogen sulphate)

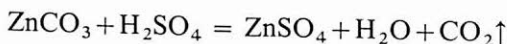
This salt is said to be acidic, since it gives a H^+ ion in solution.



ii With heavy metal hydroxides:



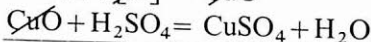
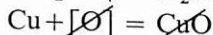
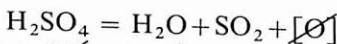
d Carbonates:



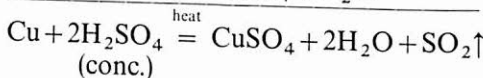
As an oxidising agent (concentrated sulphuric acid)

a With metals, e.g.

Copper:

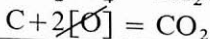
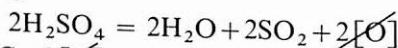


Add

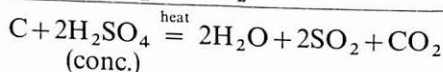


b With non-metals, e.g.

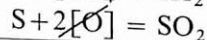
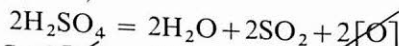
Carbon:



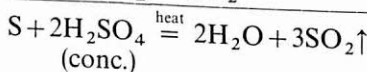
Add



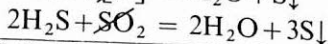
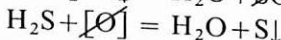
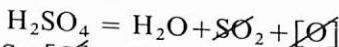
Sulphur:



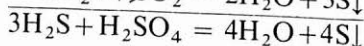
Add



c With hydrogen sulphide (cold):

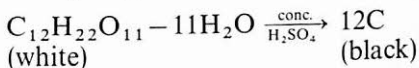


Add

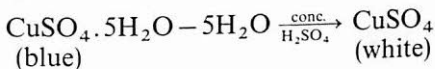


As a **dehydrating agent** (concentrated sulphuric acid). Concentrated sulphuric acid has a great affinity for water, and on dilution much heat is evolved.

i Sugar (sucrose) turns black. Sugar is a carbohydrate, i.e. it contains carbon combined with hydrogen and oxygen which are in the ratio 2:1.



ii Copper (II) sulphate crystals:



d The skin: concentrated sulphuric acid in contact with the skin removes moisture very rapidly, thus producing great heat and dehydration. The burn so produced can be very severe, and, if extensive, may penetrate to the flesh and internal organs and prove fatal.

Volatility. Sulphuric acid is non-volatile and can be used to displace volatile acids from their salts (see the preparation of hydrochloric acid, page 80 and the preparation of nitric acid, page 87).

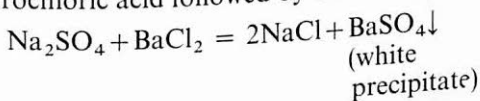
USES OF SULPHURIC ACID

Sulphuric acid is a most important industrial and laboratory chemical. Its uses are so many and varied that a comprehensive list would be impossible to produce here. The most important uses are as follows:

- a Manufacture of fertilisers.
- b Manufacture of general chemicals.
- c For cleaning metal surfaces before plating.
- d In lead accumulators.

TEST FOR SULPHURIC ACID AND SOLUBLE SULPHATES

(Soluble sulphates are substances producing SO_4^{2-} ions in solution.)
Add dilute hydrochloric acid followed by barium chloride solution.



In general, $\text{Ba}^{2+} + \text{SO}_4^{2-} = \text{BaSO}_4 \downarrow$

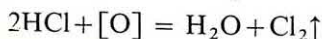
Note: The hydrochloric acid prevents the formation of barium sulphite which would form as a white precipitate if the substance under test were a sulphite SO_3^{2-} .

10 Chlorine

This is the second member of the halogen family of elements: fluorine **F**; chlorine **Cl**; bromine **Br**; iodine **I**.

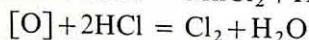
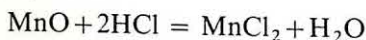
LABORATORY PREPARATION OF CHLORINE

It is prepared by the oxidation of conc. hydrochloric acid.



Oxidising agents which provide oxygen for this oxidation are:

a Manganese (IV) oxide



b Potassium permanganate

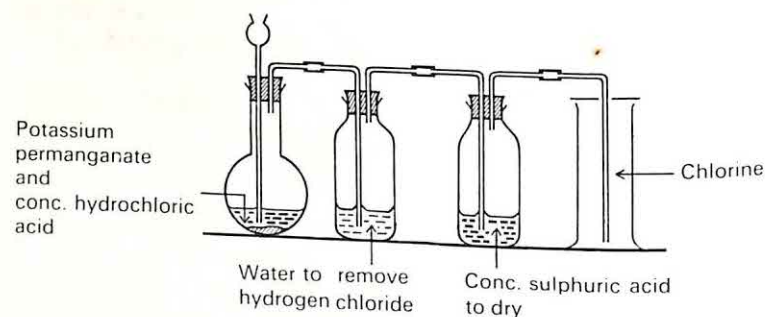
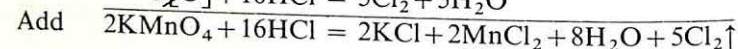
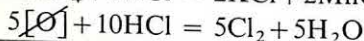
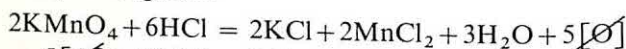
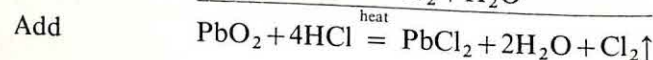
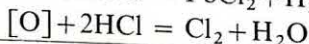
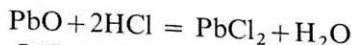
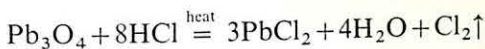


fig. 48 The preparation of chlorine

c Lead (IV) oxide



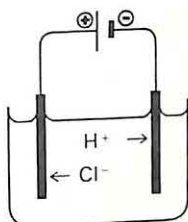
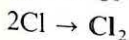
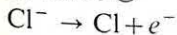
d Red lead oxide



MANUFACTURE OF CHLORINE

Chlorine may be prepared by the electrolysis of concentrated sodium chloride solution.

At anode \oplus



At cathode \ominus

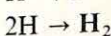
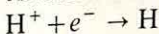
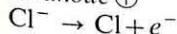


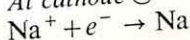
fig. 49 The electrolysis of brine

The most common industrial method is by the electrolysis of brine (conc. sodium chloride solution) using various types of electrolytic cell. The most common is the one used for the manufacture of sodium hydroxide, where chlorine is in fact a by-product.

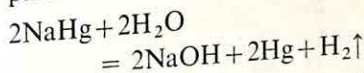
At anode \oplus



At cathode \ominus



The sodium forms an amalgam with mercury which is then passed into water.



The mercury is regenerated and recirculated.

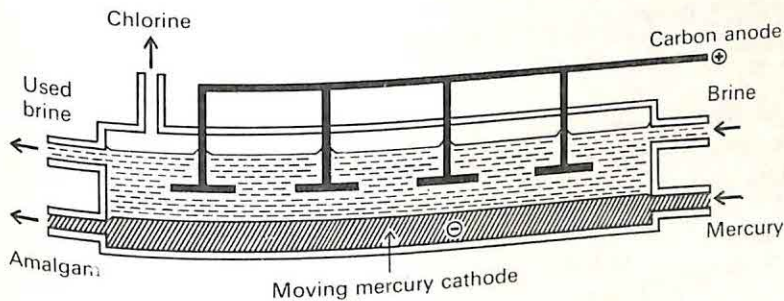


fig. 50

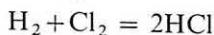
THE PROPERTIES OF CHLORINE

Physical

- a Pale green gas.
- b Offensive choking odour.
- c Sparingly soluble in water.
- d More dense than air.

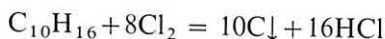
Chemical

- a Reaction with hydrogen. The gases react to form hydrogen chloride.

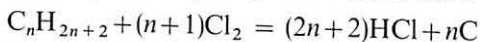


Ultra-violet light catalyses this reaction, and it becomes explosive in direct sunlight.

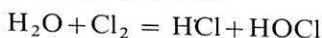
Chlorine has such an affinity for hydrogen that it can remove it from hydrogen-containing compounds, e.g. warm turpentine burns in chlorine



and a paraffin wax taper (See p. 44) continues to burn in chlorine.



- b Reaction with water and dilute alkalis.



(hypochlorous acid)

Then

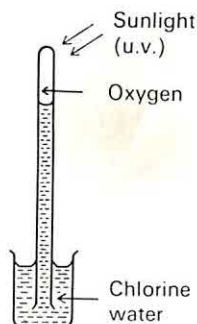
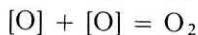
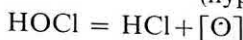
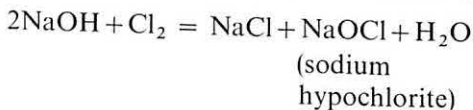


fig. 51

It is this oxygen which oxidises dyes to colourless substances, causing bleaching, and which also kills bacteria in drinking water and swimming pools.

If the water contains sodium hydroxide, the salts of the two acids are formed.



c Reaction with metals. Dry chlorine reacts with metals to form the chlorides.

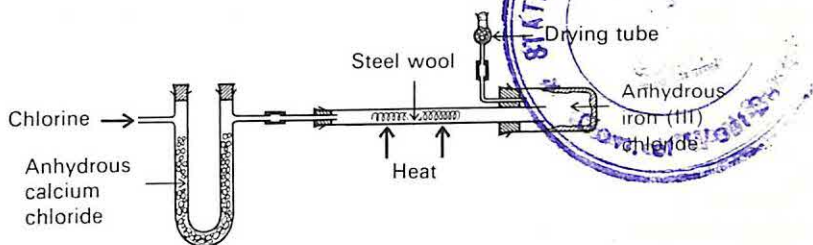
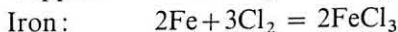
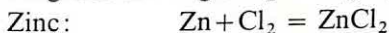
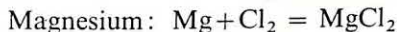
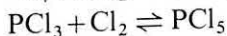
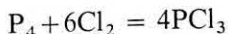


fig. 52 The preparation of anhydrous iron (III) chloride

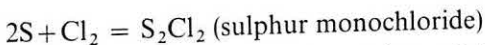
With the exception of copper (II) chloride, these cannot be made from hydrochloric acid by conventional methods, as the solution produced hydrolyses when concentrated leaving the oxide or hydroxide.

d Reaction with non-metals.

i Phosphorus:

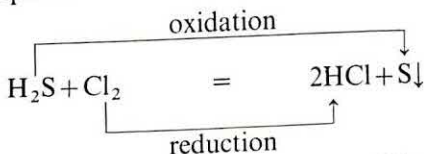


ii Sulphur:



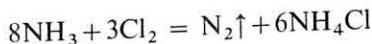
e Chlorine reacts with reducing agents, showing that it is an oxidising agent.

i Hydrogen sulphide:



ii Acidified sodium sulphite solution (see page 72)

iii Ammonia:



f Displacement of other halogens from their salts.

Potassium bromide: $2\text{KBr} + \text{Cl}_2 = 2\text{KCl} + \text{Br}_2$

Potassium iodide: $2\text{KI} + \text{Cl}_2 = 2\text{KCl} + \text{I}_2$

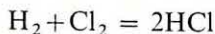
If an inch of carbon tetrachloride is added to the reaction mixture in a test-tube, the bromine forms a red-brown layer and the iodine a violet layer.

TEST FOR CHLORINE

Moist litmus in contact with chlorine gas turns red, due to the effect of the acids formed, and then bleaches due to the oxidising effect.

USES OF CHLORINE

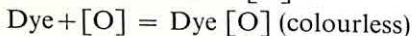
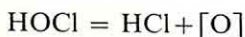
a Manufacture of hydrochloric acid.



The hydrogen and chlorine come from the electrolysis of brine.

b Chlorination of domestic water supplies and swimming pools.

c Bleaching:



d Organic chemistry. Chlorine is used in the manufacture of many well-known organic compounds, e.g.

Dichlorodiphenyl trichloroethane (D.D.T.)

Trichlorophenol (T.C.P.)

Polyvinyl chloride (P.V.C.)

Hydrogen chloride and hydrochloric acid

PREPARATION OF HYDROGEN CHLORIDE

This gas is made by the action of concentrated sulphuric acid on a suitable chloride. The reaction commences spontaneously but heat is

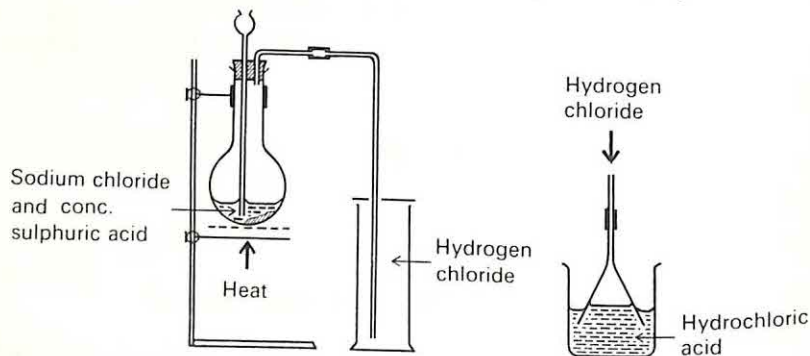
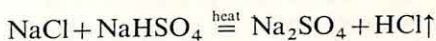
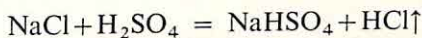


fig. 53 The preparation of hydrogen chloride and hydrochloric acid

required for its continuation.



The gas can be dissolved in water forming hydrochloric acid, but the precaution shown must be taken to prevent sucking back due to the high solubility of the gas.

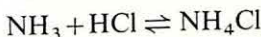
PROPERTIES OF HYDROGEN CHLORIDE

Physical

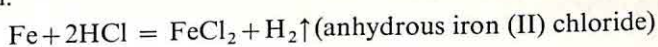
- a Colourless gas.
- b Pungent odour.
- c Fumes in moist air.
- d More dense than air.
- e Very soluble in water.

Chemical

- a Reacts with ammonia to form white fumes of ammonium chloride.

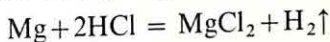


- b When it is dried and passed over heated metals the chlorides are formed.

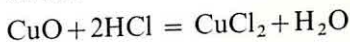


PROPERTIES OF HYDROCHLORIC ACID

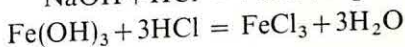
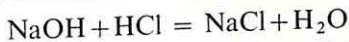
- a Turns blue litmus red.
- b Reacts with metals above hydrogen in the electrochemical series.



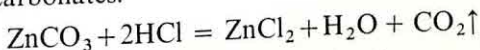
- c Reacts with basic oxides.



- d Reacts with alkalis and insoluble hydroxides.



- e Reacts with carbonates.



- f Forms insoluble chlorides with some metal salts.

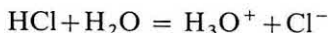
Silver chloride: $\text{AgNO}_3 + \text{HCl} = \text{HNO}_3 + \text{AgCl}\downarrow$ (white precipitate)

This is a test for the acid or for any soluble chloride when nitric acid is present in the solution. The precipitate is soluble in ammonia.

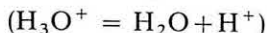
Lead (II) chloride: $\text{Pb(NO}_3)_2 + 2\text{HCl} = 2\text{HNO}_3 + \text{PbCl}_2\downarrow$
(white crystalline precipitate)

Note: Lead (II) chloride is insoluble in cold water but quite soluble in hot water.

These chemical properties are all due to the fact that hydrogen chloride, although a covalent compound, is subjected to a rearrangement of electrons when dissolved in water.



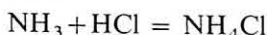
(H_3O^+ , the hydroxonium ion, is a hydrated form of a hydrogen ion.)



In a covalent solvent such as toluene this rearrangement does not take place and hydrogen chloride remains covalent. Thus many of the reactions listed above (page 81) do not take place in toluene solution, e.g.

a It does not conduct electricity. \therefore electrolysis cannot take place.

b The toluene solution gives a white precipitate of ammonium chloride when ammonia is passed in.



This reaction can take place between covalent molecules and since the ammonium chloride is not soluble in toluene, it precipitates.

c The toluene solution has no reaction with metals and little reaction with carbonates.

Chlorides

These are prepared by the normal methods of salt preparation as seen on pages 23, 24 and 79.

They are all white or colourless except where colour is introduced by the metal, e.g. copper (II) chloride is green; iron (II) chloride is green; iron (III) chloride is brown.

They are all soluble in water except:

Silver chloride – insoluble.

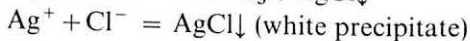
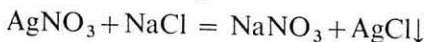
Lead (II) chloride – soluble in hot water only.

TESTS FOR CHLORIDES

In solution

Add dilute nitric acid to remove any possible traces of alkali.

Add silver nitrate solution, e.g.



The white precipitate **i** coagulates on shaking;

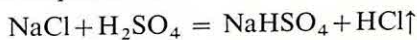
ii dissolves in ammonia;

iii darkens on exposure to light.

Solid

Either

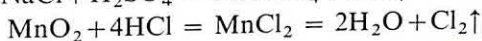
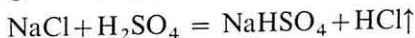
Add concentrated sulphuric acid.



Test for hydrogen chloride by mixing with ammonia.

Or

Mix with manganese (IV) oxide, add concentrated sulphuric acid and heat.



Test for chlorine with moist litmus.

11 Nitrogen and its compounds

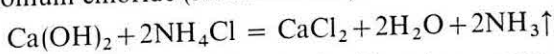
Nitrogen

There is a large percentage of nitrogen in the earth's crust. It occupies $\frac{4}{5}$ by volume of the air and is also present, in the combined state, in many substances found in animals and plants, e.g. proteins and chlorophyll. It also occurs in nitrates, e.g. Chilean saltpetre NaNO_3 .

Ammonia

LABORATORY PREPARATION OF AMMONIA

a By heating a mixture of solid calcium hydroxide (slaked lime) and solid ammonium chloride (sal ammoniac).



As the ammonia gas evolved is mixed with water vapour, it must be

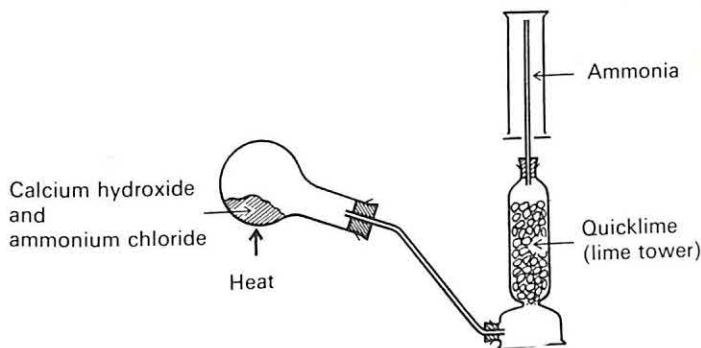
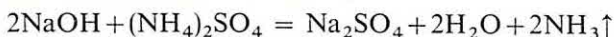


fig. 54 The preparation of ammonia

dried with calcium oxide (quicklime) in a lime tower, as conventional drying agents such as concentrated sulphuric acid and anhydrous calcium chloride react with ammonia.

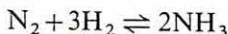
Note: Any ammonium salt, except ammonium nitrate, when heated with any alkali, produces ammonia, e.g.



b By heating concentrated ammonia solution (0.880 ammonia).

INDUSTRIAL PREPARATION OF AMMONIA

a The Haber Process



Nitrogen and hydrogen are dried and passed over an iron catalyst. The conditions for the reaction are very important and it is carried out at a temperature of 500°C and under a pressure of from 200 to 800 atmospheres.

b From ammoniacal liquor which is a by-product of the coal gas industry (see page 42).

PROPERTIES OF AMMONIA

Physical

a Colourless gas.

b Pungent, choking smell.

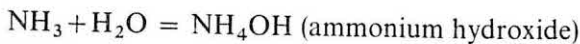
c Lighter than air.

d Very soluble in water.

1200 cm^3 of the gas will dissolve in 10 cm^3 of water at N.T.P. This high solubility may be demonstrated by the *fountain experiment* (fig. 55), which also shows that the gas is alkaline.

Chemical

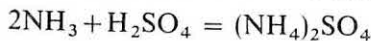
a Reaction with water



Ammonium hydroxide is an alkali.



b Reaction with acids. Ammonium salts are formed.



c Reaction with oxygen. Ammonia gas burns with a green flame in oxygen gas.

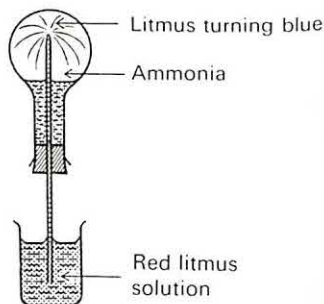
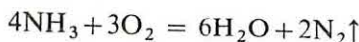
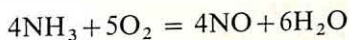


fig. 55 The fountain experiment

If a platinum catalyst is used, nitric oxide is formed.



(See industrial preparation of nitric acid, page 87.)

Ammonia can remove the oxygen from hot copper (II) oxide to produce copper, nitrogen and water, i.e. it is a *reducing agent*.

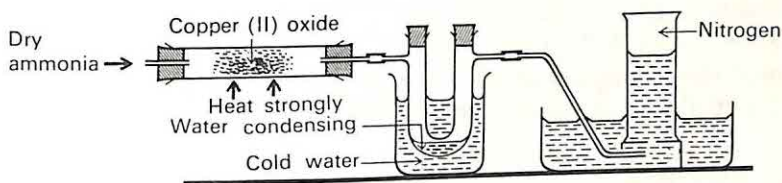
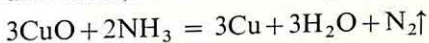
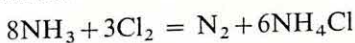


fig. 56

The products of this reaction indicate that ammonia contains only nitrogen and hydrogen atoms, i.e. it is a *hydride* of nitrogen.

d Reaction with chlorine.

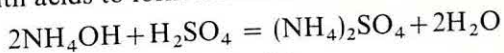


Ammonium hydroxide

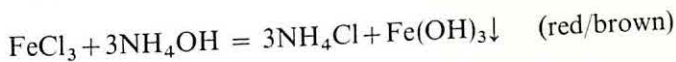
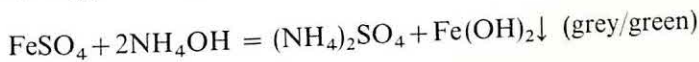
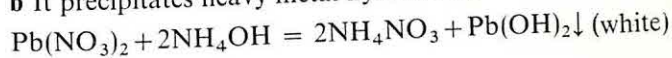
Ammonium hydroxide is prepared, as seen already, by dissolving ammonia gas in water. It is a volatile, colourless liquid, smelling of ammonia and is an alkali.

PROPERTIES OF AMMONIUM HYDROXIDE

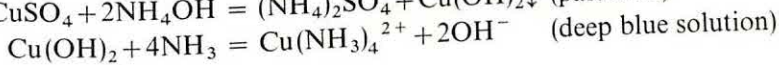
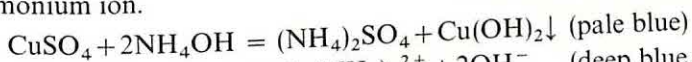
a It reacts with acids to form ammonium salts.



b It precipitates heavy metal hydroxides.



The hydroxides above are insoluble in excess ammonium hydroxide; the hydroxide of copper however dissolves in excess of ammonium hydroxide forming a deep blue solution containing the complex cuprammonium ion.



USES OF AMMONIUM HYDROXIDE

a Manufacture of nitric acid (see page 87).

b Preparation of ammonium salts.

Ammonia or
ammonium hydroxide + acid = ammonium salt + water

b Bleaching. Ammonia reacts with acidic substances in dirty fabrics and forms soluble substances which wash away easily.

d Ammonia gas liquefies easily and can be used in refrigerators to produce low temperatures by evaporation.

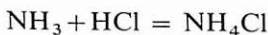
Note: Liquid ammonia which is the liquefied form of the gas must not be confused with ammonia solution (ammonium hydroxide).

TESTS FOR AMMONIA

a Smell.

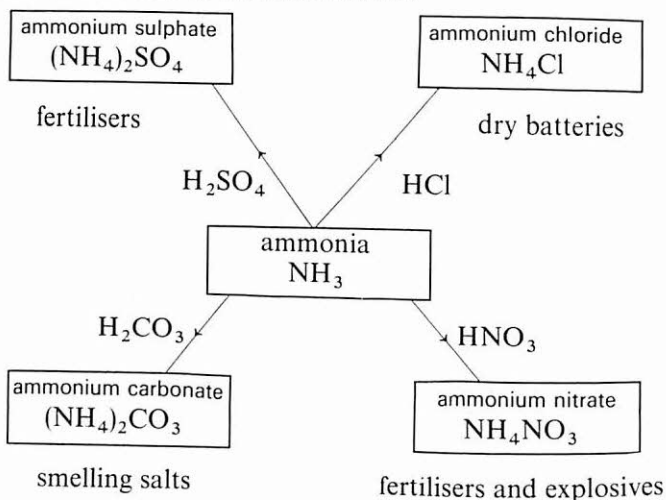
b Turns moist red litmus blue.

c Produces white fumes of ammonium chloride when in contact with hydrogen chloride gas.



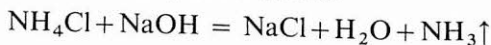
Ammonium salts

PREPARATION AND USES OF AMMONIUM SALTS

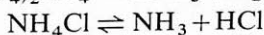
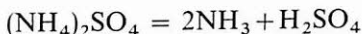


PROPERTIES OF AMMONIUM SALTS

a They react with alkalis to give ammonia.



b They decompose when heated.



Nitric acid

LABORATORY PREPARATION OF NITRIC ACID

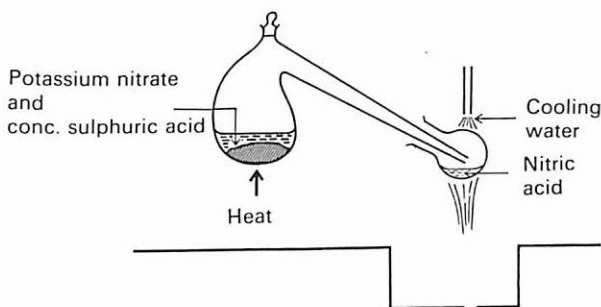
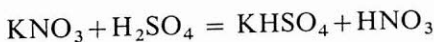


fig. 57 The preparation of nitric acid

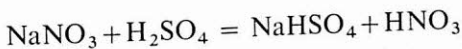
Concentrated sulphuric acid reacts with nitrates to produce nitric acid. The mixture is heated and the nitric acid vapour is condensed in a cooled flask.



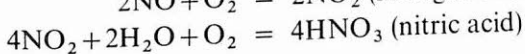
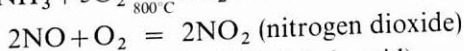
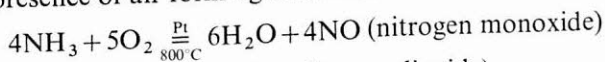
Since nitric acid vapour attacks rubber and cork, the apparatus consists entirely of glass. The traditional apparatus is a retort as shown in fig. 57. Nowadays this can be replaced by ground glass joint apparatus incorporating a Liebig condenser, which is much more efficient.

INDUSTRIAL PREPARATION OF NITRIC ACID

a Formerly nitric acid was made by a method similar to the laboratory preparation, but making use of iron retorts and Chilean saltpetre NaNO_3 .



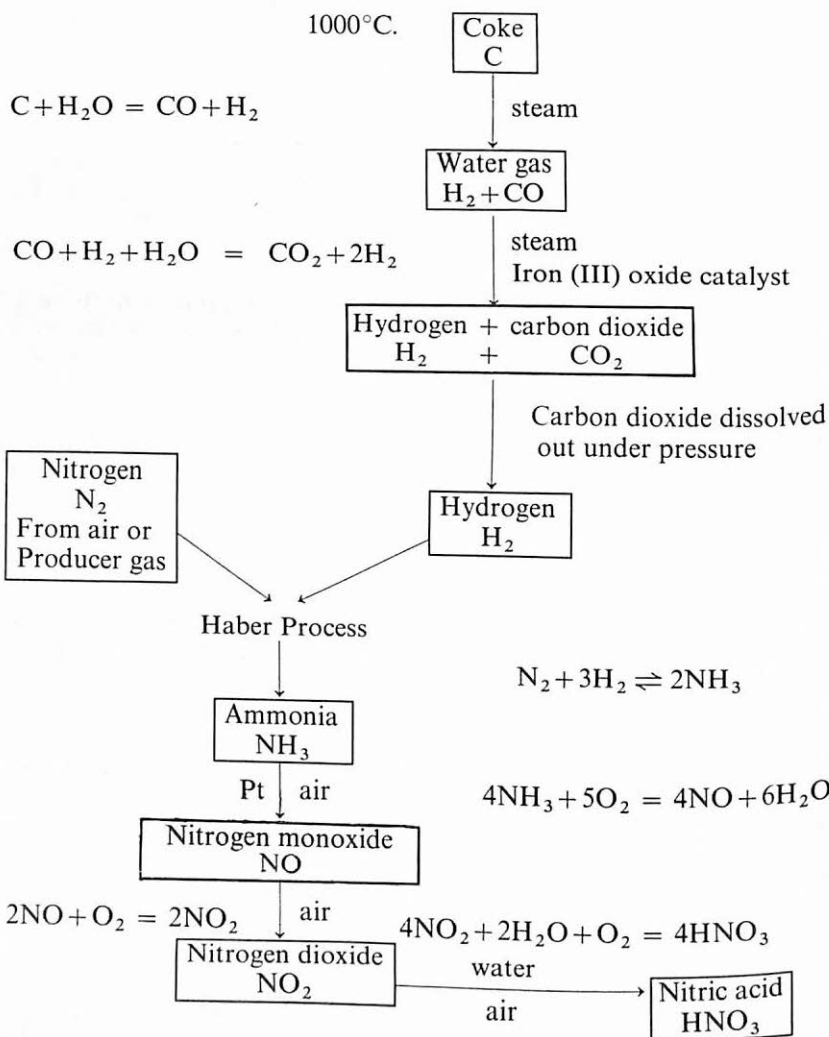
b Nitric acid is now manufactured by the catalytic oxidation of ammonia. Dry ammonia is mixed with an excess of dry air and passed over a platinum catalyst at 800°C producing nitrogen monoxide which is cooled and oxidised by more air to nitrogen dioxide. This is dissolved in water in the presence of air forming nitric acid.



This produces acid of maximum concentration 68% which is the familiar concentrated nitric acid. If a more concentrated solution is required, i.e. fuming nitric acid (97%), it is made by distillation of the 68% variety with concentrated sulphuric acid.

The following process shows how relatively simple, cheap, and easily obtained raw materials can be utilised to synthesise a very important and useful chemical.

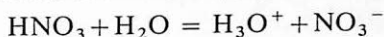
The basic raw materials in this process are coke, air and water. Other chemicals used, e.g. platinum, are not exhausted in the reaction.



PROPERTIES OF NITRIC ACID

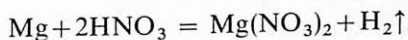
As an acid

Fuming nitric acid does not exhibit normal acid reactions until diluted.



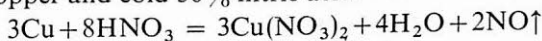
Dilute nitric acid reacts in the normal and expected way with oxides, hydroxides and carbonates of metals but due to its oxidising powers, even when dilute, it does not give hydrogen with the majority of metals.

a Action on metals. Magnesium reacts with very dilute nitric acid to give hydrogen.

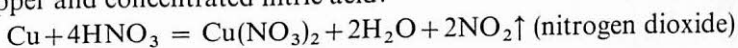


Normally however, the products are the nitrate, water and one of the oxides of nitrogen, e.g.

Copper and cold 50 % nitric acid:

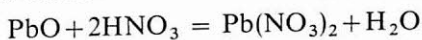


Copper and concentrated nitric acid:

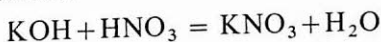


In some cases the reaction is very complex and one equation is not sufficient to explain it.

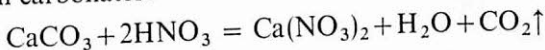
b Action on basic oxides:



c Action on hydroxides:

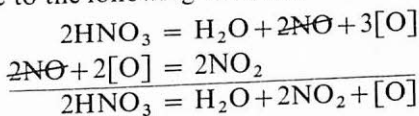


d Action on carbonates:



As an oxidising agent

This effect is due to the following reaction.



Add

Nitrogen dioxide (NO_2) is the brown gas evolved from the majority of nitric acid reactions.

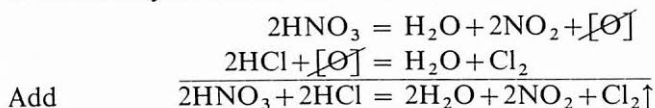
a Nitric acid reacts violently with many organic compounds and care should always be taken to avoid its accidental contact with such substances, e.g.

Warm fuming nitric acid (as prepared in the laboratory) when added to warm dry sawdust causes it to burst into flames.

b Oxidises hydrogen sulphide to sulphur. (see page 70)

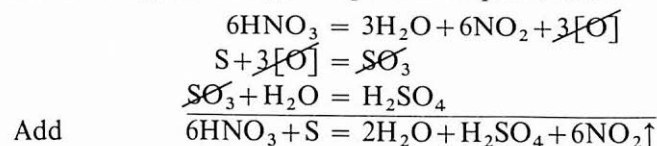
c Oxidises sulphur dioxide to sulphuric acid. (see page 72)

d Oxidises hydrochloric acid to chlorine.

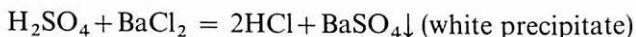


A mixture of 1 part concentrated nitric acid and 3 parts concentrated hydrochloric acid is known as *aqua regia* and has the ability to dissolve gold.

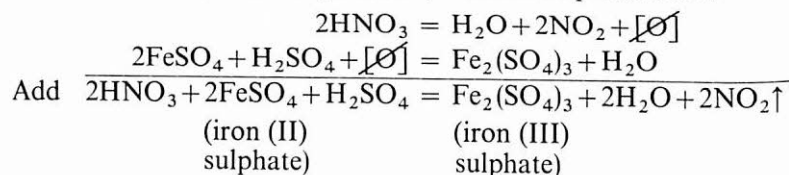
e Oxidises sulphur to sulphuric acid. When sulphur is boiled with concentrated nitric acid, brown fumes of nitrogen dioxide are evolved and the resulting solution gives a positive sulphate test.



Test



f Oxidises iron (II) compounds to iron (III) compounds. The pale green colour of iron (II) sulphate changes to yellowish-brown when nitric acid is added in the presence of dilute sulphuric acid.



Oxides of nitrogen

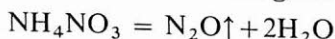
There are three important oxides.

- | | |
|-----------------------|----------------------|
| a Dinitrogen monoxide | N_2O |
| b Nitrogen monoxide | NO |
| c Nitrogen dioxide | NO_2 |

PREPARATIONS OF THE OXIDES OF NITROGEN

Dinitrogen monoxide

Action of heat on ammonium nitrate. **Take great care.**



This is a colourless gas, is soluble in cold water and can, when pure and dry, relight a glowing splint. It is commonly known as laughing gas and is used as an anaesthetic.

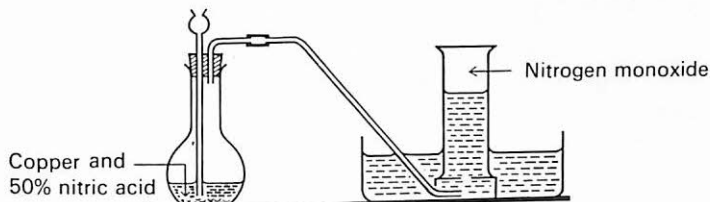
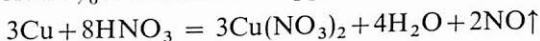


fig. 58 The preparation of nitrogen monoxide

Nitrogen monoxide

Action of cold 50% nitric acid on copper.



Nitrogen dioxide

Action of heat on lead nitrate.



The nitrogen dioxide is separated by cooling in a freezing mixture where it collects as a blue/green liquid. If this liquid is then poured into a gas jar, it evaporates forming a brown gas.

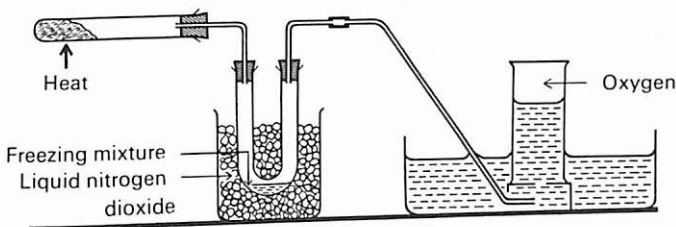


fig. 59 The preparation of nitrogen dioxide

	NITROGEN MONOXIDE	NITROGEN DIOXIDE
Colour	colourless	brown gas
Solubility	insoluble	reacts with water to give a mixture of nitric acid and nitrous acid: $\text{H}_2\text{O} + 2\text{NO}_2 = \text{HNO}_3 + \text{HNO}_2$
Acidity	neutral	acidic (see above)
Reaction with oxygen	oxidation to nitrogen dioxide $2\text{NO} + \text{O}_2 = 2\text{NO}_2$	no reaction
Reaction with iron II sulphate solution	produces dark brown addition compound: nitroso iron (II) sulphate $\text{FeSO}_4 + \text{NO} = \text{FeSO}_4 \cdot \text{NO}$ (brown substance in the brown ring test)	only slight reaction

Nitrates

These are salts of nitric acid and are prepared by normal methods of salt preparation (see pages 23 and 24).

Nitrate	Action of heat	Use
KNO_3	$2\text{KNO}_3 = 2\text{KNO}_2 + \text{O}_2\uparrow$	gunpowder
NaNO_3	$2\text{NaNO}_3 = 2\text{NaNO}_2 + \text{O}_2\uparrow$	nitric acid manufacture
NH_4NO_3	$\text{NH}_4\text{NO}_3 = 2\text{H}_2\text{O} + \text{N}_2\text{O}\uparrow$	fertilisers and explosives
$\text{Pb}(\text{NO}_3)_2$	$2\text{Pb}(\text{NO}_3)_2 = 2\text{PbO} + 4\text{NO}_2\uparrow + \text{O}_2\uparrow$	laboratory reagent
AgNO_3	$2\text{AgNO}_3 = 2\text{Ag} + 2\text{NO}_2\uparrow + \text{O}_2\uparrow$	laboratory reagent

TESTS FOR A NITRATE

The brown ring test. Make a fresh solution of iron (II) sulphate and add a crystal of the nitrate or a few drops of its solution. Shake. Add concentrated sulphuric acid carefully down the side of the tube so that it forms a layer. A brown ring forms at the junction of the layers.

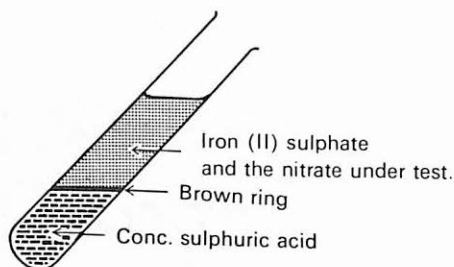
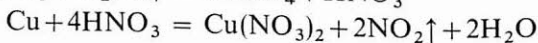
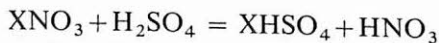


fig. 60 The brown ring test

The brown fume test. Heat the nitrate with concentrated sulphuric acid and add a small piece of copper. Brown fumes of nitrogen dioxide are evolved.



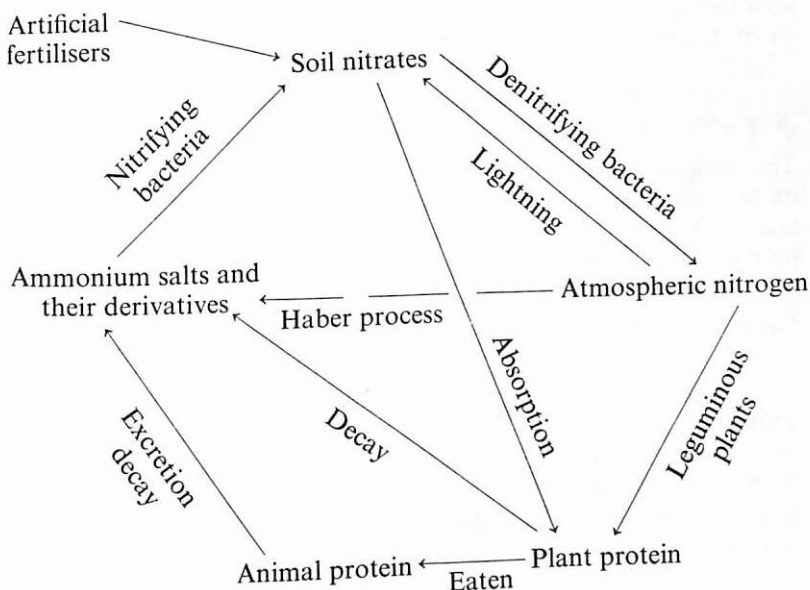
The role of nitrogen in natural processes

If good yields of food crops are to be maintained, the elements which are essential for the growth and development of plants must be present in the soil. Nitrogen is one of the most important of these elements. Others are phosphorus and potassium, with calcium, magnesium, iron and sulphur required to a lesser degree. As crops are harvested the nitrogen which they have used up is removed from the soil, and unless this is replaced, crops in subsequent seasons show a serious lack of nitrogen and eventually the soil becomes completely unproductive. Some plants are capable of making use of atmospheric nitrogen, i.e. by converting it to the required compounds, but in general the nitrogen must be replaced by some means. This can be done by adding a *fertiliser*. There are two types:

a Natural fertilisers, consisting of decayed plants and the excreta of animals (farmyard manure);

b Artificial fertilisers, consisting of chemicals or mixtures of chemicals with high nitrogen content.

THE NITROGEN CYCLE



12 The metals

GENERAL COMPARISON OF METALS AND NON-METALS

Metals	Non-metals
1 conduct electricity and heat	1 do not conduct electricity and heat
2 are malleable and ductile	2 are brittle
3 are lustrous (shiny)	3 are non-lustrous
4 form basic oxides	4 form acidic oxides
5 lose electrons to form positive ions — cations	5 gain electrons to form negative ions — anions
6 replace the hydrogen of acids to produce a metal salt	6 do not react with dilute acids
7 do not form stable hydrides	7 form stable hydrides, e.g. ammonia NH_3

The properties of the metals are summarised in the activity series (page 97).

Most of the reactions of metals and their compounds have been dealt with under other headings, e.g. action of water (pages 25–6), action of air (page 18), etc., and will not be dealt with in detail in this section.

EXTRACTION OF METALS

The method employed depends on the position in the activity series; those nearest the top require considerable energy to effect the conversion $\text{A}^+ \rightarrow \text{A}$ (compound to metal) and electrolysis is used. On the other hand metals at the bottom are easily extracted from their ores by reduction since they are quite stable.

The method of extraction for three metals are dealt with in this section.

a Sodium

Sodium is extracted by electrolysis of the fused chloride mixed with fluoride to keep the melting point low. Chlorine is given off at the anode and sodium metal at the cathode. The metal is molten and must be protected from atmospheric corrosion.



At anode \oplus
 $\text{Cl} \rightarrow \text{Cl}_2$ gas

At cathode \ominus
Na metal

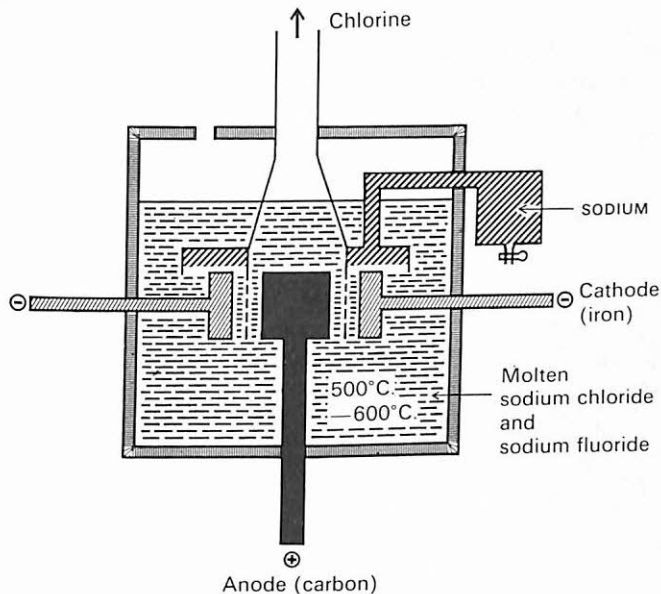
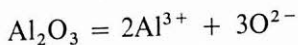


fig. 61 The extraction of sodium from sodium chloride

b Aluminium

Aluminium is made by the electrolysis of a mixture of pure molten bauxite Al_2O_3 and cryolite Na_3AlF_6 using carbon electrodes.



At anode
 $\text{O} \rightarrow \text{O}_2 \text{ gas}$

At cathode
 Al metal

The anode is burnt away easily by the oxygen produced and has to be replaced frequently.

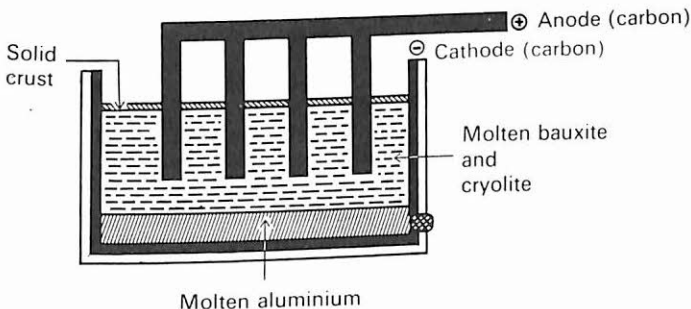


fig. 62 The extraction of aluminium from bauxite

c Iron

A mixture of iron ore [haematite (Fe_2O_3)], coke (C) and limestone (CaCO_3) is introduced into a blast furnace by means of a feeding device at the top. It is heated strongly by means of blasts of hot air coming in through the Tuyères.

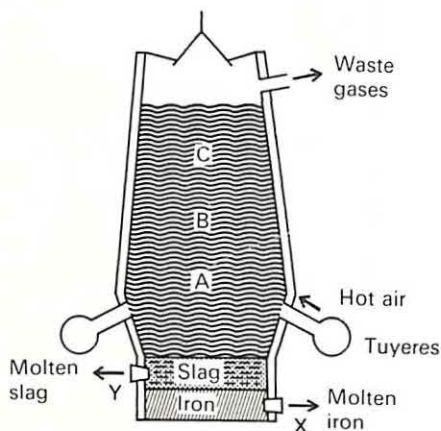
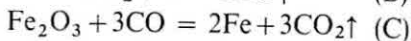
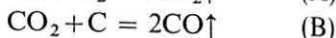
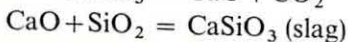
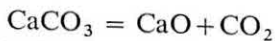


fig. 63 A blast furnace



The molten iron collects in the bottom of the furnace and can be tapped off at X when required. The limestone is decomposed to calcium oxide, which reacts with silica present in earthy materials to form calcium silicate (*slag*).



Slag also forms in the molten state and may be tapped off at Y. The iron so produced is called cast iron or pig iron and contains about 4% carbon. It is used for rough castings.

THE MANUFACTURE OF STEEL FROM IRON

There are many types of steel for different purposes containing controlled amounts of carbon and other elements, and the most important part of steelmaking is the control of the amounts.

The impurities in cast iron are removed by mixing it with more iron ore and lime in an *open hearth furnace* and blowing hot air over it for a considerable time.

The haematite (iron ore) oxidises the impurities to their oxides, some of which are volatile. The volatile oxides such as carbon dioxide and sulphur dioxide are blown out with the waste gases which are used to reheat the incoming air. Non-volatile oxides such as silica and phosphorus pentoxide combine with the lime to form a slag.



Samples are taken and analysed from time to time to ascertain if the steel is of the required quality, and various metals are added in small quantities to give it special properties. Finally the steel is tapped into ingot moulds.

Additives	Property and uses
Manganese and tungsten Chromium	hardness for drills and tools stainless steel for cutlery, etc.

In addition to these, steels with varying amounts of carbon have uses in engineering and industry in general, e.g. rods for reinforcing concrete, sheet steel, girders.

ACTIVITY SERIES OF THE METALS

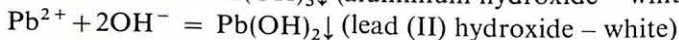
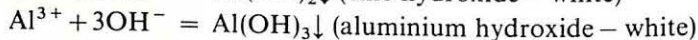
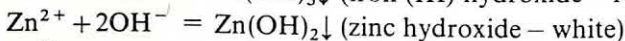
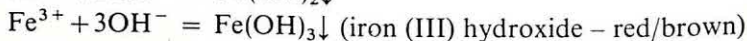
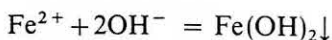
	Method of extraction	Action of air or oxygen	Action of water	Action of acids	Reduction of oxides	Action of heat on hydroxides	Action of heat on carbonates	Action of heat on nitrates					
Potassium K	electrolysis of molten salt or oxide	burn in air or oxygen	give hydrogen with cold water	give hydrogen with dilute acids	not reduced by hydrogen	no action	no action	nitrite and oxygen formed					
Sodium Na													
Calcium Ca			give hydrogen with steam when at red heat		oxide and water formed	oxide and carbon dioxide formed	oxide, an oxide of nitrogen and oxygen formed						
Magnesium Mg													
Aluminium Al	reduction of oxide	oxidise when heated in air or oxygen	no action	only attacked by oxidising acids	reduced easily by hydrogen and carbon								
Zinc Zn													
Iron Fe													
Lead Pb													
Copper Cu													

PRECIPITATION OF THE HYDROXIDES OF HEAVY METALS

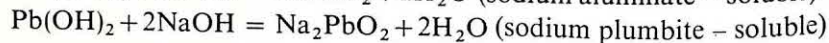
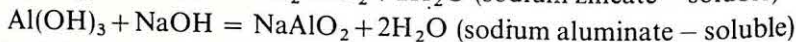
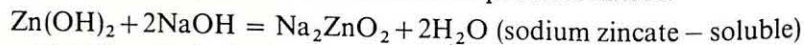
This can be effected by adding a substance containing OH^- ions in solution to a solution of the heavy metal salt, e.g.



These reactions are best shown ionically.



The last three, zinc, aluminium and lead hydroxides are all soluble in excess sodium hydroxide due to their amphoteric nature.



FLAME TESTS FOR METALS

Chlorides are generally volatile compounds and the chlorides of some metals, when vaporised in a flame, impart colour to the flame. The test is carried out by dipping a clean platinum wire into a mixture of a salt of the metal and concentrated hydrochloric acid and holding it in a Bunsen flame.

The colours produced are as follows:

Sodium	Na^+	golden yellow
Potassium	K^+	lilac
Calcium	Ca^{2+}	red
Copper	Cu^{2+}	blue/green

USES OF SOME METALS AND ALLOYS

Magnesium

Light alloys for aircraft and helicopters.
Photographic flash bulbs.

Aluminium

Bodies of buses, cars and aeroplanes and overhead cables, since it is light and strong.

Many uses in the home, e.g. domestic appliances.

Packaging and containers in general.

Zinc

Casing of dry batteries.

Galvanising iron by dipping it in molten zinc to prevent corrosion.

Copper

Wires and electrical components – in general a good conductor of electricity.

Water pipes and tanks.

Lead

Accumulators.

Glass making.

Water pipes.

Paints, e.g. red lead Pb_3O_4 and white lead $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$

Brass

Contains copper and zinc in varying combinations.

Some electrical fittings.

Screws.

Decoration.

Solder

A mixture of 3 parts lead and 2 parts tin with a low melting point.

Used to effect joins between wires in radio and other electrical equipment.

Type metal

A mixture of lead, antimony and tin.

Used in printing.

Duralumin

95% aluminium with copper, manganese and magnesium.

Used in construction instead of aluminium.



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